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FACULTY OF APPLIED SCIENCE AND ENGINEERING
SCHOOL OF ENGINEERING RESEARCH

BULLETIN NO. 6

1926

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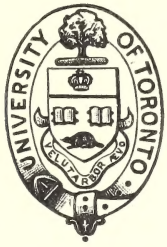

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THE APPLICATION OF CERTAIN PROJECTIONS TO THE CONSTRUCTION OF GENERAL MAPS OF CANADA

By Louis B. Stewart, *Professor of Surveying and Geodesy*

For the representation of a considerable portion of the surface of the earth numerous methods have been devised and used in the construction of maps, and among the best of these are to be included the different modifications of the conical projection with two standard parallels. It is here proposed to examine some of these modes of representation with a view to determining their adaptability to maps of the Dominion of Canada.

In all the modifications of the projection to be examined the parallels of latitude are represented by arcs of circles having a common centre, and the meridians by straight lines radiating from the same centre. Also, the scale is true along the two standard parallels, situated near the northern and southern limits of the map. The scale in longitude is therefore slightly reduced between the standard parallels, and enlarged outside of them. Various additional assumptions may be made, giving maps suited for special purposes. Thus, it may be assumed that areas shall be correctly shown; or, that all small portions shall be shown in their true forms.

An obvious advantage of these projections is that they may be easily constructed. If the scale of the map is not too large the parallels may be drawn by the aid of beam compasses; and, the degrees of longitude having been laid off along the standard parallels, the meridians may then be drawn by joining the points of division by straight lines. If the scale is large the standard parallels may be constructed by means of the rectangular coordinates of their points of intersection with the meridians, the axes of coordinates being the central meridian and lines at right angles to it through the points of intersection of the parallels.

Other advantages are: the meridians and parallels intersect at right angles; the scale is the same at all points on a parallel, either in latitude or longitude, and therefore the scale error, or the distortion, does not increase with increase of longitude from the centre of the map, as is the case with some projections that have been extensively used. These projections are therefore well adapted for maps covering a wide range in longitude, and at the same time having a considerable extent in latitude.

For the sake of comparison brief descriptions of the Polyconic and Bonne's projections will be given at the end of this account.

The following modifications of the type projection will be considered in turn:

(1) The scale in latitude is to be true at all points, and the standard parallels are to be selected arbitrarily.

(2) The scale in latitude is to be true at all points, and the maximum scale error in longitude between the standard parallels is to be equal, with opposite sign, to that of either extreme parallel.

(3) The area of any portion of the map is to be correctly shown. This projection is known as Albers' Equivalent, or Equal-Area, Projection.

(4) All small portions of the map shall be shown in their true forms. This gives Lambert's Conformal Projection.

In order to institute a comparison between these projections the following quantities will be determined in each case:

The scale errors in latitude and longitude;

The error in the representation of areas;

The error in the representation of directions at a point.

The following notation will be used:

ϕ will denote the latitude of a parallel;

ϕ_1 and ϕ_2 those of the southern and northern standard parallels;

ϕ' and ϕ'' those of the extreme parallels;

ω the longitude of a meridian; reckoned from the central meridian of the map;

θ the angle at the centre of a developed parallel corresponding to a given value of ω;

r the radius of a developed parallel;

n the ratio $\theta : \omega$, known as the "constant of the cone";

ρ the radius of curvature of the meridian at a point in given latitude;

N the length of the normal at a point, terminated in the axis of rotation of the terrestrial spheroid;

P the radius of a parallel of latitude;

m the length of a given meridian arc.

Convenient expressions for ρ N and P are as follows:

$$\rho = \frac{a(1-e^2)}{(1-e^2 \sin^2 \phi)^{\frac{3}{2}}} \tag{1}$$

$$N = \frac{a}{(1-e^2 \sin^2 \phi)^{\frac{1}{2}}} \tag{2}$$

$$P = N \cos \phi \tag{3}$$

in which a denotes the radius of the equator, and e the eccentricity of the elliptic meridian. Substituting

$$\sin \psi = e \sin \phi \tag{4}$$

these become

$$\rho = a(1-e^2) \sec^3 \psi \tag{5}$$

$$N = a \sec \psi \tag{6}$$

$$P = a \sec \psi \cos \phi \tag{7}$$

For the Clarke spheroid of 1866:

$$\log a \text{ (in miles)} = 3.5980536$$

$$\log e = \bar{2}.9152513$$

$$\log (1-e^2) = \bar{1}.9970504$$

The length of a meridian arc may be found by means of the expression:

$$\begin{aligned} m = {} & [1.83919449]\Delta\phi \text{ (in degrees)} \\ & -[1.3043545] \cos 2\phi_0 \sin \Delta\phi \\ & +[\bar{2}.3301509] \cos 4\phi_0 \sin 2\Delta\phi \\ & -[\bar{5}.45093] \cos 6\phi_0 \sin 3\Delta\phi + \end{aligned} \tag{8}$$

in which—

$\Delta\phi$ denotes the difference of latitude of the extremities of the arc, and

ϕ_0 the mean of the extreme latitudes.

The numbers in rectangular brackets are the logarithms of numerical coefficients.

For a short meridian arc—less than 1°—the following expression may be used:

$$m = \rho.\Delta\phi \sin 1'' \tag{9}$$

$\Delta\phi$ being the amplitude of the arc in seconds, and ρ the radius of curvature at its middle point.

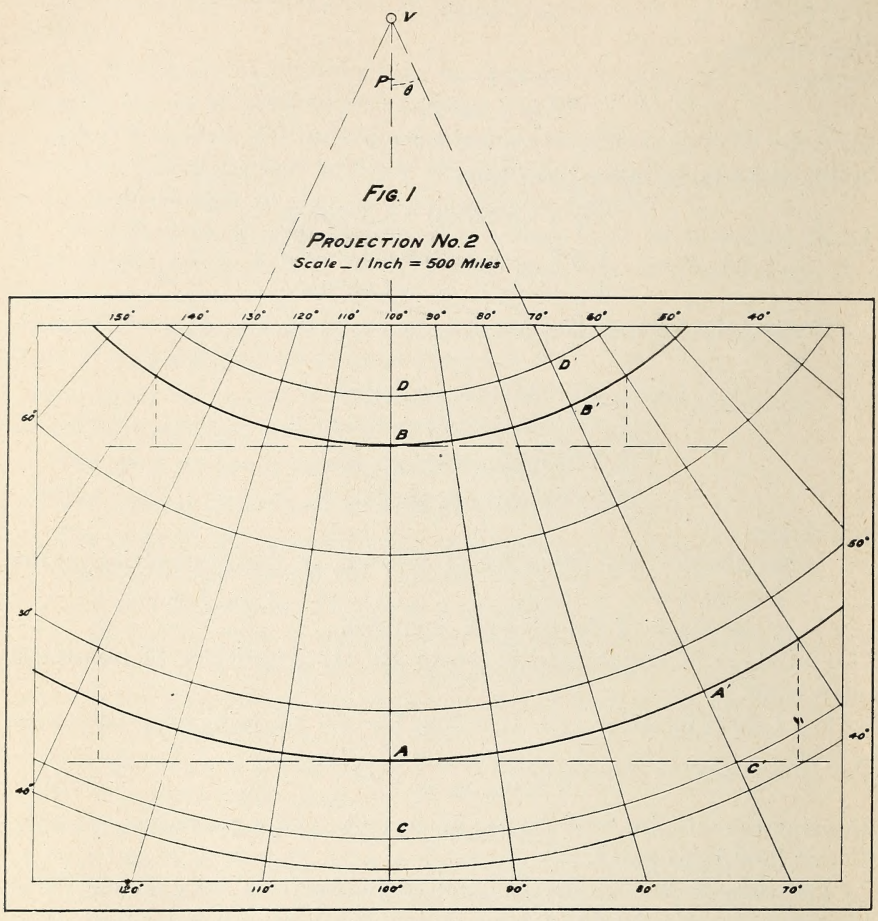
The Supplement to the Manual of Instructions for the Survey of Dominion Lands contains a table giving, for every 10′ of latitude from 42° to 70°, the values of the logarithms of $\rho \sin 1''$ (ρ being there denoted by R) $N \sin 1''$ and $P \sin 1''$, the unit being the Gunter's chain. The log. of either of these quantities in miles may be found by adding to the tabular quantity

$$\log \frac{1}{80 \sin 1''} = 3.4113351.$$

The table on p. 11 below, giving the lengths of degrees of latitude from 40° to 70°, may be used for finding the length of a long arc, the fractional degrees being found by eq. (9).

We shall proceed to the investigation of the projections enumerated above.

(1) The scale in latitude is true at all points, and the standard parallels are selected arbitrarily.



In Fig. 1 AA' and BB' are the standard parallels, their radii being r_1 and r_2, P_1 and P_2 denoting their true radii. Then we have

$$\frac{VA}{VB}=\frac{AA'}{BB'}=\frac{N_1\cos\phi_1.\omega}{N_2\cos\phi_2.\omega}=\frac{P_1}{P_2}$$

$$\therefore \quad \frac{VA}{VA-VB}=\frac{P_1}{P_1-P_2}$$

or $$\frac{r_1}{m}=\frac{P_1}{P_1-P_2}$$

or $$r_1=\frac{P_1 m}{P_1-P_2} \qquad (10)$$

m denoting the length of the meridian arc AB. Also

$$r_2 = r_1 - m \tag{11}$$

Similarly, the radius of any developed parallel is

$$r = r_1 \pm m' \tag{12}$$

m' being the length of the corresponding meridian arc.

Again,

$$AA' = r_1\theta = P_1\omega$$

so that

$$n = \frac{\theta}{\omega} = \frac{P_1}{r_1} = \frac{P_1 - P_2}{m} \tag{13}$$

Also, denoting the scale ratios in latitude and longitude by σ and σ', respectively, we have

$$\sigma = 1$$

$$\sigma' = \frac{r\theta}{P\omega} = n\frac{r}{P} = \frac{P_1 - P_2}{m} \cdot \frac{r}{P} \tag{14}$$

Also the area scale is given by the expression

$$\frac{r dr d\theta}{\rho d\phi \,.\, P d\omega}$$

But $dr = \rho d\phi$, and $d\theta = n d\omega$, $\therefore$ this expression becomes

$$\frac{rn}{P} = \sigma';$$

so that σ' is also the area scale, which is otherwise evident.

To investigate the local misrepresentation of direction at a point let us consider an infinitesimal portion of a line drawn upon the surface of the earth and having the azimuth α, and assume that a meridian is drawn through one extremity, and a line perpendicular to the meridian through the other extremity, thus forming a small triangle, the lengths of whose sides are $\rho d\phi$ and $P d\omega$, respectively; so that we have

$$\tan \alpha = \frac{P d\omega.}{\rho d\phi}$$

Then, if α' denote the angle on the map corresponding to α, we have

$$\tan \alpha' = \frac{\sigma' P d\omega}{\sigma \rho d\phi} = \frac{\sigma'}{\sigma} \tan \alpha \tag{15}$$

An expression for $\alpha' - \alpha$ may be obtained in the form of a series Eq. (15) is of the form

$$\tan x = p \tan y,$$

which by expansion in series gives

$$x - y = q \sin 2y + \tfrac{1}{2}q^2 \sin 4y + \tfrac{1}{3}q^3 \sin 6y$$

in which

$$q = \frac{p-1}{p+1}$$

Applying this, we have

$$\alpha'-\alpha=\frac{\sigma'-\sigma}{\sigma'+\sigma}\sin 2\alpha+\tfrac{1}{2}\left(\frac{\sigma'-\sigma}{\sigma'+\sigma}\right)^2\sin 4\alpha+$$

If $\alpha=45°$ the first term of this series has its maximum value, the second term vanishes, and the third—as well as each succeeding term that does not vanish—is extremely small, so that the maximum value o $\alpha'-\alpha$ in seconds is, very approximately:

$$\alpha'-\alpha=\frac{\sigma'-\sigma}{(\sigma'+\sigma)\sin 1''} \tag{16}$$

In the present case this becomes

$$a'-\alpha=\frac{\sigma'-1}{(\sigma'+1)\sin 1''} \tag{17}$$

In order to determine the latitude, between those of the standard parallels, for which the scale error in longitude is a maximum we have

$$\frac{d\sigma'}{d\phi}=0, \text{ or } n\frac{d}{d\phi}\left(\frac{r}{P}\right)=0.$$

But $$\frac{d}{d\phi}\left(\frac{r}{P}\right)=\frac{P\frac{dr}{d\phi}-r\frac{d\phi}{dP}}{P^2};$$

$\therefore$ the condition for a maximum is:

$$P\frac{dr}{d\phi}=r\frac{dP}{d\phi}$$

Then, as $$r=r_1-m$$

$\therefore$ $$\frac{dr}{d\phi}=-\frac{dm}{d\phi}=-\rho.$$

Also $$P=a\cos\phi\,(1-e^2\sin^2\phi)^{-\frac{1}{2}}$$

$\therefore$ $$\frac{dP}{d\phi}=ae^2\sin\phi\cos^2\phi(1-e^2\sin^2\phi)^{-\frac{3}{2}}$$

$$-a\sin\phi\,(1-e^2\sin^2\phi)^{-\frac{1}{2}}$$

$$=\frac{ae^2\sin\phi\cos^2\phi-a\sin\phi(1-e^2\sin^2\phi)}{(1-e^2\sin^2\phi)^{\frac{3}{2}}}$$

$$=-\frac{a(1-e^2)\sin\phi}{(1-e^2\sin^2\phi)^{\frac{3}{2}}}$$

$$=-\rho\sin\phi$$

$\therefore$ the condition for a maximum becomes

$$\rho N\cos\phi=(r_1-m)\rho\sin\phi$$

or $$\tan\phi=\frac{N}{r_1-m}=\frac{N}{r}. \tag{18}$$

This equation must be solved by trials.

The coordinates of the intersections of the meridians and parallel may be computed by means of the equations:

$$\theta = n\omega \quad x = r \sin \theta \qquad (19)$$
$$y = r(1 - \cos \theta)$$

The following table gives the length in miles of 1° of latitude for different latitudes.

Lat.	Length of 1°	Lat.	Length of 1°
°	m	°	m
40	68.99917	55	69.18039
41	69.01131	56	69.19181
42	69.02351	57	69.20306
43	69.03575	58	69.21414
44	69.04801	59	69.22502
45	69.06029	60	69.23570
46	69.07256	61	69.24616
47	69.08482	62	69.25639
48	69.09704	63	69.26637
49	69.10921	64	69.27609
50	69.12132	65	69.28555
51	69.13335	66	69.29471
52	69.14529	67	69.30361
53	69.15711	68	69.31219
54	69.16882	69	69.32046
55		70	

We shall now apply the above projection to the construction of a map of the Dominion, by assuming

$$\phi' = 42° \quad \phi'' = 70°$$

and the extreme longitudes to be 55° and 141° west. The latitudes of the standard parallels are also assumed to be:

$$\phi_1 = 45°, \quad \phi_2 = 60°.$$

By eq. (10), and the above table, we find

$$r_1 = 3548.3829\text{m}$$
$$r_2 = 2511.2187\text{m}$$

Also, by eq. (13)

$$n = 0.791123.$$

Also, by eq. (14)—

$$\sigma' = 1.00722, \text{ for lat. } 42°$$
$$\sigma' = 1.05811, \text{ for lat. } 70°.$$

These are also the area scales at the extreme latitudes.

The latitude of the parallel, between the two standard parallels, at which the scale ratio in longitude is a maximum is, eq. (18):

$$\phi = 52° \; 56' \; 05''$$

and for this latitude

$$\sigma' = 0.9914455$$

For this latitude we also find—eq. (17):

$$\alpha' - \alpha = = -14' \; 46''.04$$

At latitude 63° we find

$$\sigma' = 1.010086$$

so that up to latitude 63° the scale error will barely exceed one per cent.

By assuming the latitudes of the standard parallels differently a different distribution of scale error may be obtained.

(2) The maximum scale error between the standard parallels is to be equal, with opposite sign, to that of the extreme parallels.

Let z denote the length VP, P being the projection of the pole, and m' and m'' the lengths of the meridian arcs between the extreme parallels and the pole.

Then, the scale ratios of these parallels being equal, we have

$$\frac{(z+m')\theta}{P'\omega} = \frac{(z+m'')\theta}{P''\omega};$$

whence

$$z = \frac{m'P'' - m''P'}{P' - P''}; \tag{20}$$

which determines z.

Again, to find the latitude corresponding to the maximum scale error between the standard parallels, we have, for a parallel near the centre of the map

$$1 - \sigma' = 1 - \frac{n(z+m),}{P}$$

or

$$\sigma' = \frac{n(z+m)}{P}. \tag{21}$$

We now differentiate this with reference to ϕ and equate to zero, thus

$$\frac{d\sigma'}{d\phi} = n \frac{P\frac{dm}{d\phi} - (z+m)\frac{dP}{d\phi}}{P^2} = 0$$

$$\therefore \quad P\frac{dm}{d\phi} = (z+m)\frac{dP}{d\phi}.$$

Then as

$$\frac{dm}{d\phi} = -\rho \text{ and } \frac{dP}{d\phi} = -\rho \sin \phi$$

this becomes

$$P\rho = (z+m)\rho \sin \phi,$$

or

$$N \cos \phi = (z+m) \sin \phi,$$

or

$$N_0 \cot \phi_0 - m_0 = z, \tag{22}$$

which gives the latitude corresponding to the maximum scale error This equation must be solved by trials.

Again, the scale ratio being the same, with opposite sign, on this parallel and either extreme parallel, we have

$$1-\frac{n(z+m_0)}{P_0}=\frac{n(z+m')}{P'}-1$$

whence

$$\frac{1}{n}=\frac{z+m_0}{2P_0}+\frac{z+m'}{2P'} \tag{23}$$

which gives n.

Again, for the standard parallels

$$\frac{n(z+m_1)}{P_1}=\frac{n(z+m_2)}{P_2}=1$$

or

$$P_1-nm_1=nz, \tag{24}$$

and

$$P_2-nm_2=nz;$$

by which ϕ_1 and ϕ_2 may be determined by trials.

This modification of (1) may now be applied to the construction of a map of Canada by assuming again the extreme latitudes to be

$$\phi'=42^\circ\ \phi''=70^\circ$$

We must first find m' and m'' By means of eq. (8) we find—

$$m''=1387^m.5858$$

and by adding to this the lengths of degrees of latitude contained in the table, p. 11 we find— $m'=3324^m.6545$.

Then by table in D.L.S. Manual—

$$\log P'=3.4697861,$$
$$\log P''=3.1334070.$$

Then eq. (20) gives

$$z=268.5985.$$

Then by eq. (22)—

$$\phi_0=57^\circ\ 49'\ 20''.17.$$

The value of n then follows by (23):

$$n=0.8334627\ldots;$$

for which the scale ratio is found by (21):

$$\sigma'=0.9847151$$
$$=1-0.0152849$$

As a check the scale ratio is found for either extreme parallel to be

$$\sigma'=1.0152848$$

The maximum error in a direction for latitude ϕ_0 is found by (17) to be

$$\alpha'-\alpha=-26'\ 28''.5;$$

and this is the maximum for the whole map.

The latitudes of the standard parallels are, by (24)

$$\phi_1=46^\circ\ 53'\ 39''.15$$
$$\phi_2=66^\circ\ 53'\ 34''.81.$$

(3) Albers' Equivalent, or Equal-Area, Projection.

A brief development of the theory of this projection may not be out of place.

The scale ratios in latitude and longitude may be thus expressed

$$\sigma = -\frac{dr}{\rho d\phi} \quad \sigma' = \frac{rd\theta}{Pd\omega} = \frac{nr}{N\cos\phi} \tag{25}$$

Also the condition for equivalence of areas is:

$$\sigma\sigma' = 1$$

or
$$-\frac{dr}{\rho d\phi} \cdot \frac{nr}{N\cos\phi} = 1$$

or
$$nrdr = -\rho N\cos\phi d\phi \tag{26}$$

By (1) and (2) this becomes

$$nrdr = -\frac{a^2(1-e^2)}{(1-e^2\sin^2\phi)^2}\cos\phi d\phi$$

or
$$rdr = -\frac{a^2(1-e^2)}{n} \cdot \frac{\cos\phi d\phi}{(1-e^2\sin^2\phi)^2}$$

Therefore
$$\frac{r^2}{2} = -\frac{a^2(1-e^2)}{n}\int\frac{\cos\phi d\phi}{(1-e^2\sin^2\phi)^2}$$

If now r_0 denote the value of r when $\phi = 0$ this becomes

$$r^2 - r_0^2 = -\frac{2a^2(1-e^2)}{n}\int_0^\phi \frac{\cos\phi d\phi}{(1-e^2\sin^2\phi)^2}$$

If then the earth were a sphere having the radius R, and β denote the value of the latitude on this supposition, the right-hand member of the last expression would become:

$$\frac{2R^2}{n}\int_0^\beta \cos\beta d\beta = -\frac{2R^2}{n}\sin\beta.$$

We may therefore define β by equating the two expressions, which gives

$$R^2\sin\beta = a^2(1-e^2)\int_0^\phi \frac{\cos\phi d\phi}{(1-e^2\sin^2\phi)^2}$$

Therefore, expanding and integrating each term separately, we have

$$R^2\sin\beta = a^2(1-e^2)\int_0^\phi (1+2e^2\sin^2\phi+3e^4\sin^4\phi + 4e^6\sin^6\phi+)\cos\phi d\phi$$

$$= a^2(1-e^2)\left(\sin\phi+\frac{2e^2}{3}\sin^3\phi+\frac{3e^4}{5}\sin^5\phi + \frac{4e^6}{7}\sin^7\phi+\right).$$

R may be determined by assuming that when $\phi = \frac{\pi}{2}$, β also $= \frac{\pi}{2}$, which

gives

$$R^2 = a^2(1-e^2)\left(1+\frac{2e^2}{3}+\frac{3e^4}{5}+\frac{4e^6}{7}+\right) \tag{27}$$

R is the radius of the sphere having the same surface area as that of the spheroid. For the Clarke spheroid of 1866—

$$\log R(\text{in metres}) = 6.80420742$$
$$\log R(\text{in miles}) = 3.59756243$$

β is then given by the expression:

$$\sin\beta = \sin\phi \frac{1+\frac{2e^2}{3}\sin^2\phi+\frac{3e^4}{5}\sin^4\phi+\frac{4e^6}{7}\sin^6\phi+}{1+\frac{2e^2}{3}+\frac{3e^4}{5}+\frac{4e^6}{7}+}$$

$$= \sin\phi\left\{1-\frac{2e^2}{3}\cos^2\phi-\left(\frac{7}{45}\cos^2\phi+\frac{3}{5}\sin^2\phi\cos^2\phi\right)e^4\right.$$
$$-\left(\frac{64}{945}\cos^2\phi+\frac{6}{35}\sin^2\phi\cos^2\phi+\frac{4}{7}\sin^4\phi\cos^2\phi\right)e^6$$
$$\left.+\text{ etc.}\right\} \tag{28}$$

β is termed the "authalic", or equal-area, latitude. The difference $\phi-\beta$ may be computed by the expression:

$$\phi-\beta = 467''.0129\sin 2\phi - 0''.4494\sin 4\phi$$
$$+0''.0005\sin 6\phi— \tag{29}$$

A table is given in Special Publication No. 67 of the U.S. Coast and Geodetic Survey which contains values of $\phi-\beta$ for 30′ intervals of latitude from 0° to 90°,

The expression for r may then be written:

$$r^2 = r_0^2 - \frac{2R^2}{n}\sin\beta \tag{30}$$

The constants n and r_0 must now be determined. Introducing the condition that the scale shall be true along the standard parallels, we have

$$r_1 = \frac{N_1\cos\phi_1}{n} \quad r_2 = \frac{N_2\cos\phi_2}{n} \tag{31}$$

and substituting these values of r_1 and r_2 in the expression for r we have

$$r_0^2 - \frac{2R^2}{n}\sin\beta_1 = \frac{N_1^2\cos^2\phi_1}{n^2} = \frac{P_1^2}{n^2}$$
$$r_0^2 - \frac{2R^2}{n}\sin\beta_2 = \frac{N_2^2\cos^2\phi_2}{n^2} = \frac{P_2^2}{n^2}$$

Then subtracting we find

$$\frac{2R^2}{n}\left(\sin\beta_2-\sin\beta_1\right)=\frac{P_1^2-P_2^2}{n^2}$$

whence

$$n=\frac{P_1^2-P_2^2}{2R^2\,(\sin\beta_2-\sin\beta_1)} \tag{32}$$

Again, from the general expression for r we have

$$r_1^2=r_0^2-\frac{2R^2}{n}\sin\beta_1$$

whence

$$r^2-r_1^2=\frac{2R^2}{n}\,(\sin\beta_1-\sin\beta)$$

or

$$r^2=r_1^2+\frac{2R^2}{n}(\sin\beta_1-\sin\beta). \tag{33}$$

Similarly

$$r^2=r_2^2+\frac{2R^2}{n}(\sin\beta_2-\sin\beta) \tag{34}$$

For convenience of computation the expressions for r may be written

$$\frac{r^2}{R^2}=\left(\frac{r_1^2}{R^2}+\frac{2}{n}\sin\beta_1\right)-\frac{2}{n}\sin\beta \tag{35}$$

$$\frac{r^2}{R^2}=\left(\frac{r_2^2}{R^2}+\frac{2}{n}\sin\beta_2\right)-\frac{2}{n}\sin\beta \tag{36}$$

The scale ratio for any parallel is

$$\sigma'=\frac{nr}{P}, \tag{37}$$

and that for a meridian at any point:

$$\sigma=\frac{1}{\sigma'}=\frac{P}{nr} \tag{38}$$

To find the latitude of the parallel, between the standard parallels, for which σ is a maximum, we have

$$\frac{d\sigma}{d\phi}=\frac{1}{n}\,\frac{r\dfrac{d}{d\phi}(N\cos\phi)-N\cos\phi\,\dfrac{dr}{d\phi}}{r^2};$$

so that, equating to zero, the condition for a maximum is

$$r\frac{d}{d\phi}(N\cos\phi)=N\cos\phi\,\frac{d}{d\phi}r.$$

But $\dfrac{d}{d\phi}(N\cos\phi)=\cos\phi\,\dfrac{dN}{d\phi}-N\sin\phi$

$$= -\cos\phi \frac{a}{2} (1-e^2 \sin^2\phi)^{-\frac{3}{2}}(-2e^2 \sin\phi \cos\phi)$$

$$-N \sin\phi$$

$$= \frac{ae^2 \sin\phi \cos^2\phi - a \sin\phi (1-e^2 \sin^2\phi)}{(1-e^2 \sin^2\phi)^{\frac{3}{2}}}$$

$$= -\frac{a(1-e^2) \sin\phi}{(1-e^2 \sin^2\phi)^{\frac{3}{2}}} = -\rho \sin\phi$$

Also, by (26)
$$\frac{dr}{d\phi} = -\frac{\rho N \cos\phi}{nr},$$

Therefore the condition for a maximum becomes

$$r\rho \sin\phi = \frac{N \cos\phi \rho N \cos\phi}{nr}$$

$$= \frac{\rho N^2 \cos^2\phi}{nr}$$

or
$$\tan\phi \sec\phi = \frac{N^2}{nr^2} \tag{39}$$

By eq. (16) we have for the maximum error in direction at a point

$$\alpha' - \alpha = \frac{\frac{1}{\sigma} - \sigma}{\left(\frac{1}{\sigma} + \sigma\right) \sin 1''} = \frac{1-\sigma^2}{(1+\sigma^2) \sin 1''} \tag{40}$$

We now apply this projection to the construction of a map of the Dominion, by assuming as before

$$\phi' = 42^\circ \quad \phi'' = 70^\circ$$

We shall also take the standard parallels in the latitudes

$$\phi_1 = 45^\circ \quad \phi_2 = 65^\circ$$

By eq. (32) we find

$$n = 0.8067798 \ldots$$

Also by eq's, (31)

$$r_1 = 3479.5229$$
$$r_2 = 2081.8885$$

The latitude for which σ is a maximum is found by a series of approximations, using eq. (39), to be:

$$56^\circ\ 17'\ 05''.04;$$

for which we find

$$\sigma = 1.01539135 \ldots$$

Also
$$\sigma' = 0.9848418 \ldots$$
$$= 1 - 0.0151582. \ldots$$

We also find—eq. (40)—for the same latitude:

$$\alpha' - \alpha = -52'\ 30''.28.$$

The following table gives the value of r for each degree of the map computed by eq. (36), from which are found the length of each degree of the developed meridian. The errors of the latter are found by comparison with the lengths given in the table, p. 11.

Lat.	r	Length of 1°	Error	
°	m	m	m	%
42	3685.8212	68.5672	−0.4563	−0.66
43	3617.2540	68.7695	−0.2662	−0.39
44	3548.4845	68.9616	−0.0864	−0.13
45	3479.5229	69.1430	0.0827	0.12
46	3410.3799	69.3137	0.2411	0.35
47	3341.0362	69.4725	0.3877	0.56
48	3271.5937	69.6193	0.5223	0.76
49	3201.9744	69.7530	0.6438	0.93
50	3132.2214	69.8734	0.7521	1.09
51	3062.3480	69.9789	0.8453	1.22
52	2992.3691	70.0396	0.9243	1.34
53	2922.2995	70.1438	0.9867	1.43
54	2852.1557	70.2000	1.0312	1.49
55	2781.9557	70.2380	1.0576	1.53
56	2711.7177	70.2552	1.0634	1.54
57	2641.4625	70.2513	1.0482	1.51
58	2571.2112	70.2226	1.0085	1.46
59	2500.9886	70.1684	0.9434	1.36
60	2430.8202	70.0861	0.8504	1.23
61	2360.7341	69.9725	0.7263	1.05
62	2290.7616	69.8244	0.5680	0.82
63	2220.9372	69.6384	0.3720	0.54
64	2151.2988	69.4103	0.1342	0.19
65	2081.8885	69.1349	−0.1506	−0.22
66	2012.7536	68.8062	−0.4885	−0.70
67	1943.9474	68.4185	−0.8851	−1.28
68	1875.5289	67.9625	−1.3497	−1.95
69	1807.5664	67.4307	−1.8898	−2.73
70	1740.1357			

(4) The Lambert Conformal Projection.

A brief development of the theory of this projection is also given here.

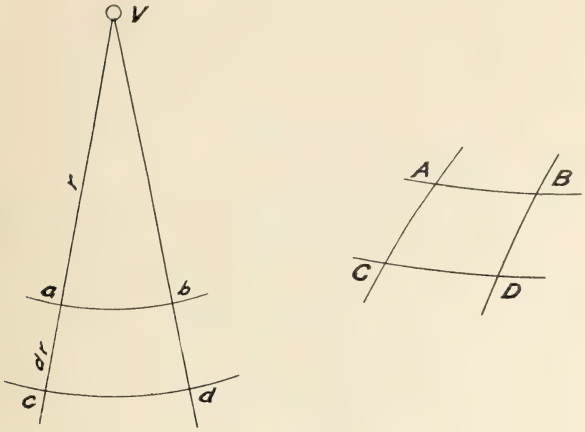


FIG. 2

In Fig. 2 $ABCD$ represents an elementary quadrilateral on the surface of the earth, bounded by meridians and parallels of latitude, and $abcd$ is its representation on the map.

If u denotes the co-latitude of AB we have

$$BD = \rho du = \frac{a(1-e^2)\,du}{(1-e^2\cos^2 u)^{\frac{3}{2}}}$$

$$AB = N \sin u d\omega = \frac{a \sin u d\omega}{(1-e^2\cos^2 u)^{\frac{1}{2}}}$$

Then, as the representation is conformal

$$\frac{bd}{ab} = \frac{BD}{AB}$$

or

$$\frac{dr}{nrd\omega} = \frac{a(1-e^2)du}{(1-e^2\cos^2 u)^{\frac{3}{2}}} \cdot \frac{(1-e^2\cos^2 u)^{\frac{1}{2}}}{a \sin u d\omega}$$

$\therefore$

$$\frac{1}{n}\frac{dr}{r} = \frac{(1-e^2)du}{\sin u(1-e^2\cos^2 u)}$$

$$= \frac{1}{\sin u}\left(1 - e^2\frac{1-\cos^2 u}{1-e^2\cos^2 u}\right)du$$

$$= \frac{du}{\sin u} - \frac{e^2 \sin u du}{1-e^2\cos^2 u}. \qquad (41)$$

Then, resolving into partial fractions, this becomes

$$\frac{1}{n}\frac{dr}{r} = \frac{du}{\sin u} - \frac{e^2 \sin u du}{2(1+e\cos u)} - \frac{e^2 \sin u du}{2(1-e\cos u)}.$$

Then integrating, we have

$$\frac{1}{n}\log r = \log\tan\frac{u}{2} + \frac{e}{2}\log(1+e\cos u) - \frac{e}{2}\log(1-e\cos u) + \frac{1}{n}\log k$$

the last term being the constant of integration. This may be written

$$\log\frac{r}{k} = n\log\left\{\tan\frac{u}{2}\left(\frac{1+e\cos u}{1-e\cos u}\right)^{\frac{e}{2}}\right\}$$

or

$$r = k\left(\tan\frac{u}{2}\right)^{n}\left(\frac{1+e\cos u}{1-e\cos u}\right)^{\frac{ne}{2}}$$

If now an angle z be assumed, such that

$$\tan\frac{z}{2} = \tan\frac{u}{2}\left(\frac{1+e\cos u}{1-e\cos u)}\right)^{\frac{e}{2}};$$

and also an angle q, such that

$$\cos q = e\cos u \tag{42}$$

we shall have

$$\left(\frac{1+e\cos u}{1-e\cos u}\right)^{\frac{1}{2}} = \left(\frac{1+\cos q}{1-\cos q}\right)^{\frac{1}{2}} = \cot\tfrac{1}{2}q;$$

so that

$$\left(\cot\frac{q}{2}\right)^{e} = \left(\frac{1+e\cos u}{1-e\cos u}\right)^{\frac{e}{2}}$$

and

$$\tan\frac{z}{2} = \tan\frac{u}{2}\left(\cot\frac{q}{2}\right)^{e}; \tag{43}$$

$\therefore$

$$r = k\left(\tan\frac{z}{2}\right)^{n} \tag{44}$$

A close approximation to the angle z may be found by computing the geocentric latitude ϕ' by the equation:

$$\tan\phi' = (1-e^2)\tan\phi; \tag{45}$$

then approximately

$$z = 90^\circ - \phi' \tag{46}$$

The value of n may now be found by assuming the scale to be true along the two selected standard parallels. Then making use of the fact that the lengths of two arcs of these parallels, each having the longitude ω, are proportional to their representations, we have

$$\frac{n\omega r_1}{n\omega r_2} = \frac{N_1\cos\phi_1\cdot\omega}{N_2\cos\phi_2\cdot\omega}$$

or

$$\frac{r_1}{r_2} = \frac{N_1\cos\phi_1}{N_2\cos\phi_2}$$

or
$$\left(\frac{\tan \frac{1}{2}z_1}{\tan \frac{1}{2}z_2}\right)^n = \frac{N_1 \cos \phi_1}{N_2 \cos \phi_2} = \frac{P_1}{P_2}.$$

Then taking log's. and solving for n, we have

$$n = \frac{\log P_1 - \log P_2}{\log \tan \frac{z_1}{2} - \log \tan \frac{z^2}{2}} \tag{47}$$

An expression for k may now be found by equating the length of an arc of a standard parallel and that of its representation, thus

$$nr_1\omega = P_1\omega$$

or
$$nk\left(\tan \frac{z_1}{2}\right)^n = P_1$$

or
$$k = \frac{P_1}{n\left(\tan \frac{z_1}{2}\right)^n} = \frac{P_2}{n\left(\tan \frac{z_2}{2}\right)^n} \tag{48}$$

The collected equations then are:

$$\cos q = e \cos u = e \sin \phi$$

$$\tan \frac{z}{2} = \tan \frac{u}{2}\left(\cot \frac{q}{2}\right)^e = \tan (45° - \tfrac{1}{2}\phi)\left(\cot \frac{q}{2}\right)^e$$

$$n = \frac{\log P_1 - \log P_2}{\log \tan \frac{z_1}{2} - \log \tan \frac{z_2}{2}}$$

$$k = \frac{P_1}{n\left(\tan \frac{z_1}{2}\right)^n} = \frac{P_2}{n\left(\tan \frac{z_2}{2}\right)^n}$$

$$r = k\left(\tan \frac{z}{2}\right)^n$$

Eq's. (19) may be used in plotting a parallel of latitude by coordinates.

The scale ratio of any parallel is evidently:

$$\sigma' = \frac{n\omega r}{P\omega} = \frac{nr}{P}; \tag{49}$$

see eq. (14). Also, as the projection is conformal

$$\sigma = \sigma' \tag{50}$$

The area scale is

$$\sigma\sigma' = \sigma^2 = \left(\frac{nr}{P}\right)^2; \tag{51}$$

Eq, (16) also gives $\alpha' - \alpha = 0$; (52)

so that directions are correctly represented at a point.

To find the latitude for which the scale error, between the standard parallels, is a maximum, we have, as on p. 10 the necessary condition:

$$P\frac{dr}{d\phi} = r\frac{dP}{d\phi}$$

Then, by (41)

$$\frac{dr}{d\phi} = nr\left(\frac{e^2 \cos\phi}{1-e^2 \sin^2\phi} - \frac{1}{\cos\phi}\right)$$

Also on p. 10 it was shown that

$$\frac{dP}{d\phi} = -\rho \sin\phi.$$

Therefore the above condition becomes

$$Pn\left(\frac{e^2 \cos\phi}{1-e^2 \sin^2\phi} - \frac{1}{\cos\phi}\right) = -\rho \sin\phi$$

or $$n\,\frac{a\cos\phi}{(1-e^2\sin^2\phi)^{\frac{1}{2}}} \cdot \frac{e^2\cos^2\phi - 1 + e^2\sin^2\phi}{\cos\phi(1-e^2\sin^2\phi)} = -\rho\sin\phi$$

or $$-n\,\frac{a(1-e^2)}{(1-e^2\sin^2\phi)^{\frac{3}{2}}} = -\rho\sin\phi$$

or $$n\rho = \rho\sin\phi$$

or $$\sin\phi = n, \qquad (53)$$

the required condition.

Applying this projection to the same data as in the previous case, viz.:

$$\phi' = 42°, \phi'' = 70°$$

$$\phi_1 = 45°, \phi_2 = 65°$$

we obtain the following results:

Eq. (47)— $n = 0.8234698\ldots$

Eq. (31)— $r_1 = 3409.0005$

$r_2 = 2039.6931.$

Also the latitude for which the scale error is a maximum is—eq. (53):

$$\phi = \sin^{-1} n = 55°\ 26'\ 01''.16;$$

and for this latitude we find—eq. (49):

$$\sigma = \sigma' = 0.984733\ldots$$
$$= 1 - 0.015\ldots$$

Also the area scale—eq. (51):

$$\sigma^2 = 0.969699$$
$$= 1 - 0.030.\ldots$$

Directions are correctly represented—eq. (52).

The properties of projections (3) and (4) are evidently mutually

exclusive, as it is impossible for any projection to embody, for all parts of the map, the two conditions:

$$\sigma\sigma' = 1, \text{ and } \sigma = \sigma',$$

unless, at the same time, it were possible that—

$$\sigma = 1, \text{ and } \sigma' = 1.$$

This could only be realized, however, if the surface of a sphere or a spheroid were developable.

The following table gives, for Lambert's projection, the value of r for each degree of latitude between 42° and 70°, from which the lengths of the individual degrees of latitude follow. The errors of the latter are found by comparison with the lengths given in the table, p. 11.

Lat.	r	Length of 1°	Error	
°	m	m	m	%
42	3617.0780	69.5744	0.5509	0.80
43	3547.5036	69.3532	0.3175	0.46
44	3478.1504	69.1499	0.1019	0.15
45	3409.0005	68.9644	−0.0959	−0.14
46	3340.0361	68.7972	−0.2754	−0.40
47	3271.2389	68.6478	−0.4370	−0.63
48	3202.5911	68.5166	−0.5804	−0.84
49	3134.0745	68.4040	−0.7052	−1.02
50	3065.6705	68.3096	−0.8117	−1.17
51	2997.3609	68.2341	−0.8992	−1.30
52	2929.1268	68.1775	−0.9678	−1.40
53	2860.9493	68.1402	−1.0169	−1.47
54	2792.8091	68.1227	−1.0461	−1.51
55	2724.6864	68.1251	−1.0553	−1.53
56	2656.5613	68.1482	−1.0436	−1.51
57	2588.4131	68.1924	−1.0107	−1.46
58	2520.2207	68.2586	−0.9555	−1.38
59	2451.9621	68.3474	−0.8776	−1.27
60	2383.6147	68.4593	−0.7764	−1.12
61	2315.1554	68.5956	−0.6506	−0.94
62	2246.5598	68.7576	−0.4988	−0.72
63	2177.8022	68.9463	−0.3201	−0.46
64	2108.8559	69.1628	−0.1133	−0.16
65	2039.6931	69.4090	0.1235	0.18
66	1970.2841	69.6870	0.3923	0.57
67	1900.5971	69.9986	0.6950	1.00
68	1830.5985	70.3463	1.0341	1.49
69	1760.2522	70.7327	1.4122	2.04
70	1689.5195			

THE POLYCONIC PROJECTION

In this projection each parallel of latitude is assumed to be the base of a right circular cone, tangent to the surface of the earth along the

parallel, and whose vertex is consequently on the axis of the earth produced. When the cone is developed the parallel becomes a circular arc whose radius—

$$r = N \cot \phi, \tag{54}$$

The central meridian of the map is represented by a straight line, on which the true lengths of the degrees of latitude are laid off to scale. Each parallel is then described about its own centre, and the degrees of longitude laid off on it correctly to scale. Through the points of division thus found the remaining meridians are drawn,

As the scale is true along any parallel we have the relation:

$$r\theta = P\omega;$$

or
$$\theta N \cot \phi = \omega N \cos \phi;$$

so that
$$\theta = \omega \sin \phi; \tag{55}$$

and
$$n = \frac{\theta}{\omega} = \sin \phi. \tag{56}$$

n has therefore a different value for each parallel.

The parallels may be drawn, on maps of large scale, by means of coordinates computed by (19).

The scale of the map is thus correct along the central meridian, and along the parallels, but the scale in latitude increases considerably with increase of distance from the central meridian. The meridians, in general, are represented by curved lines, and they do not intersect the parallels at right angles.

The increase of scale in latitude is given approximately by the expression (See U.S.C. and G. Survey Spec. Pub. No, 57):

$$E = 0.01\left(\frac{\omega \cos \phi}{8.1}\right)^2 \tag{57}$$

in which ω is expressed in degrees. By means of this equation we find the scale error at some points as follows:

$\phi = 49°$, $\angle = 125°$: $E = 0.0410$ or 4.10%.
$\phi = 55°\ 26'$, $\angle = 130°$: $E = 0.0442$ or 4.42%.
$\phi = 70°$, $\angle = 141°$: $E = 0.02997$ or 2.997%.

Let us now find, for latitude 49°, the range of longitude for which the scale error in latitude amounts to 0.01. Placing $E = 0.01$ in (57) and solving for ω we find

$$\omega = 8.1 \sec \phi$$
$$= 12°.346 \ldots$$

for latitude 49°. This projection should therefore not be used for maps covering a wider range in longitude than about 25°. It is, however, within these limits, a very useful projection, on account of the ease with which it can be constructed; extensive tables being available which

are applicable to any part of the world, and which greatly facilitate the work of the cartographer.

BONNE'S PROJECTION

This is a modification of the simple conical projection. The scale is true along a central parallel, and the degrees of latitude are laid off correctly along the central meridian which is represented by a straight line. The radius of the central parallel:

$$r_0 = N_0 \cot \phi_0, \tag{58}$$

ϕ_0 being its latitude, and the remaining parallels are circular arcs described about the same centre, so that the radius of any parallel:

$$r = r_0 \pm m, \tag{59}$$

m being its distance, measured along the central meridian, from the central parallel. The degrees of longitude are then laid off truly along each parallel and the points of division joined, as in the polyconic projection. We have then, for any parallel, the relation

$$r\theta = N \cos \phi . \omega$$

whence

$$\theta = \frac{N}{r} \omega \cos \phi \tag{60}$$

The points of intersection of the meridians and parallels may be plotted by means of coordinates, computed by the equations:

$$\begin{aligned} x &= r \sin \theta \\ y &= r_0 - r \cos \theta \end{aligned} \tag{61}$$

the origin being the point of intersection of the central meridian and the central parallel.

A point in favour of this projection is that it is equal-area; the main objection to it is on account of the obliquity of the intersections of the meridians and parallels at points distant from the central meridian. The divergence from a right angle at any such intersection may be found by the expression

$$\tan \psi = \frac{\pi}{180} (\theta - \omega \sin \phi), \tag{62}$$

θ and ω being expressed in degrees. For latitude 70° and longitude 141° ($\omega = 41°$) this gives $\psi = 5° 54' 20''$.

Also the scale error in latitude at this point is

0.005 or 0.5 per cent.

At the point whose geographical coordinates are

$$\phi = 49°, L = 125°$$

the scale error in latitude is zero, and

$$\psi = 1° 43' 09''.6.$$

The scale errors in latitude thus appear to be small. This advantage, however, is offset by the fact that the obliquity of the intersections of the meridians and parallels causes the two diagonals of a quadrilateral formed by two meridians and two parallels, which should have the same length, to have widely different lengths. This fault does not exist in the four modifications of the conical projection with two standard parallels, considered above, in which the intersections are all right-angled.

REINFORCED CONCRETE POLES

By Peter Gillespie, *Professor of Civil Engineering*,
and F. E. Wilson, *Research Assistant*

Diagrams for Strength in Bending

The first eight diagrams herewith were constructed to facilitate the rapid determination of the bending strength of reinforced concrete poles of various cross-sections, solid and hollow. It will be observed that d everywhere is the overall diameter and that p is the ratio of area of metal to the total area of the cross-section. The ratio q indicates the position of the reinforcement in the cross-section. Three different values of q are provided for on each diagram. In all cases, the weight of the pole has been neglected.

The bending strength of symmetrical reinforced concrete poles is proportional to the cube of the diameter, or

$$M = Rd^3$$

where R is a numerical modulus depending on amount and position of reinforcement, permissible stresses and the modular ratio n. For any given case, it is therefore desirable to determine R after which the moment of resistance M may be readily computed.

The original computations are in general laborious, the equations being long and involved. In the case of the hollow circular pole, for example, it can be shown, Fig. 9, that

$$np\pi = \tan\theta - \theta \tag{1}$$

$$k = \tfrac{1}{2}[(1-2q)\,(1-\cos\theta)] + q \tag{2}$$

$$\frac{f_s}{f_c} = \frac{1-k-q}{k}\,n \tag{3}$$

$$\text{and } \frac{M}{f_c d^3} = \frac{q(1-2q)^2(1-k-q)\,(2\theta - \sin 2\theta + 2np\pi)}{4k(1+\cos\theta)} \tag{4}$$

The first step in the calculations was to find simultaneous values of p and θ. For this purpose equation (1) was employed, θ being assumed, and p solved for. From this, a p, θ curve was constructed. From equation (2) k for any assumed values of p and q was determined. This gave the family of curves in the upper left corner of the diagram. Equation (3) gave the family of curves in the upper right corner of the diagram. From equation (4) the group of curves in the lower left

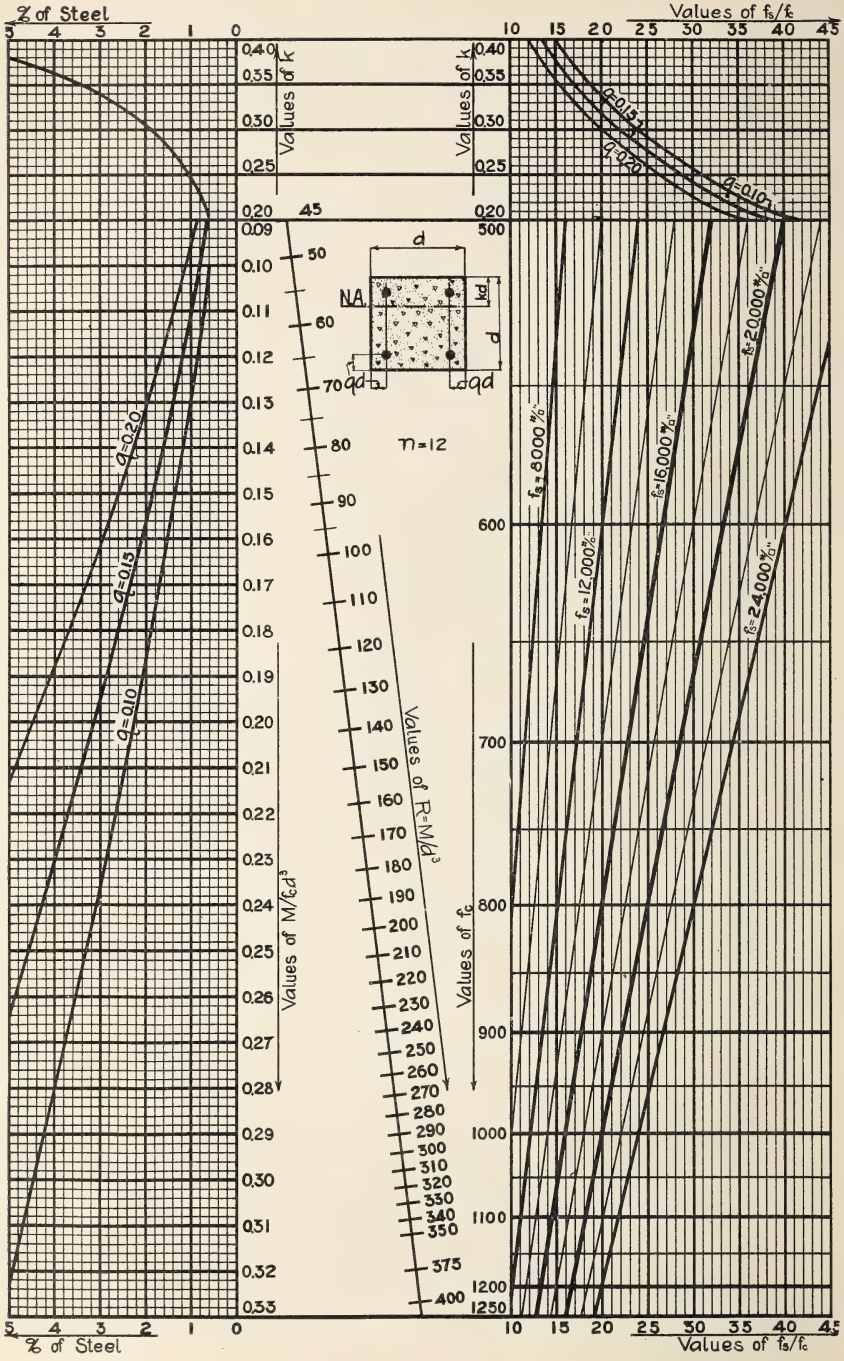


Fig. 1. Solid Square—Four Individual Rods.

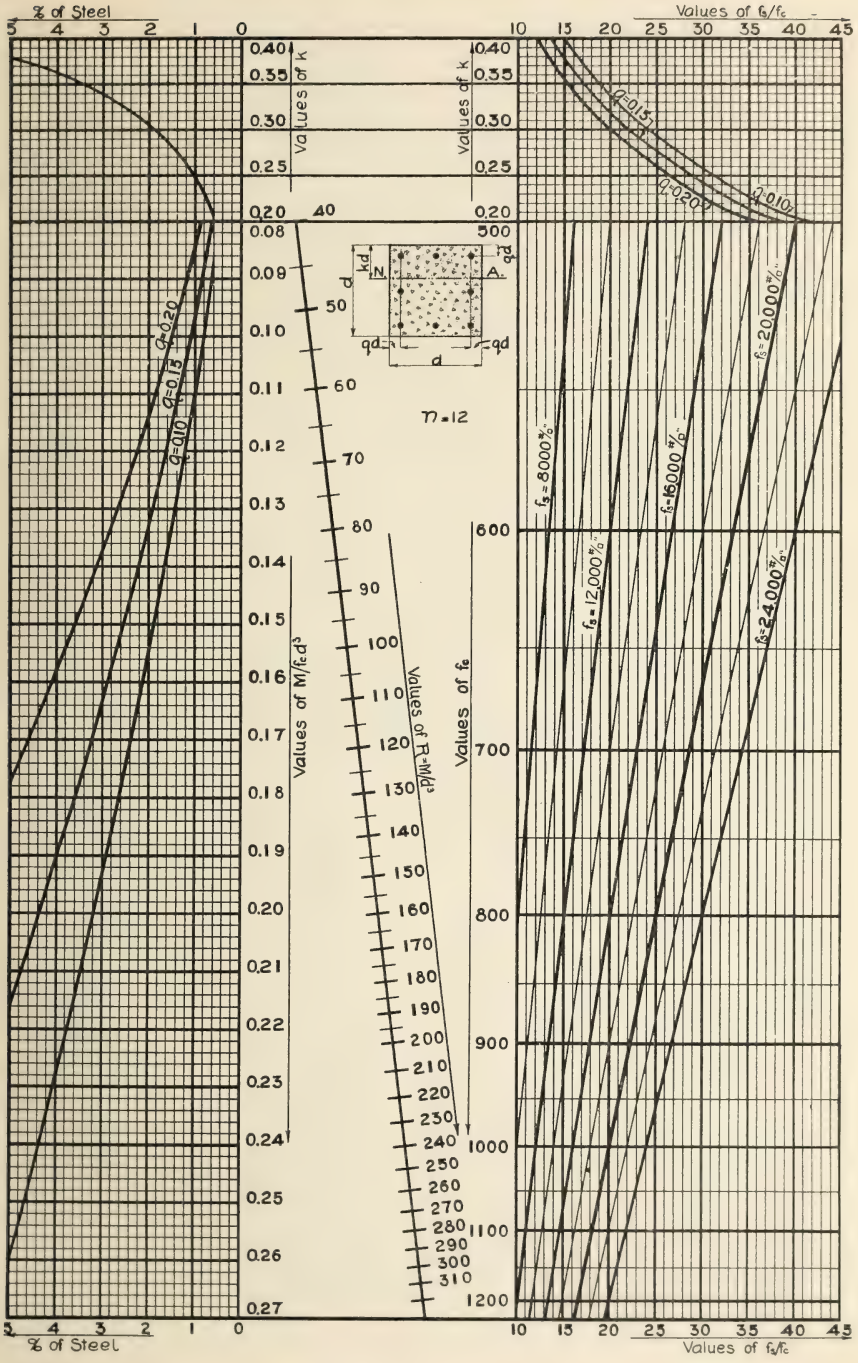


Fig. 2. Solid Square—Eight Individual Rods.

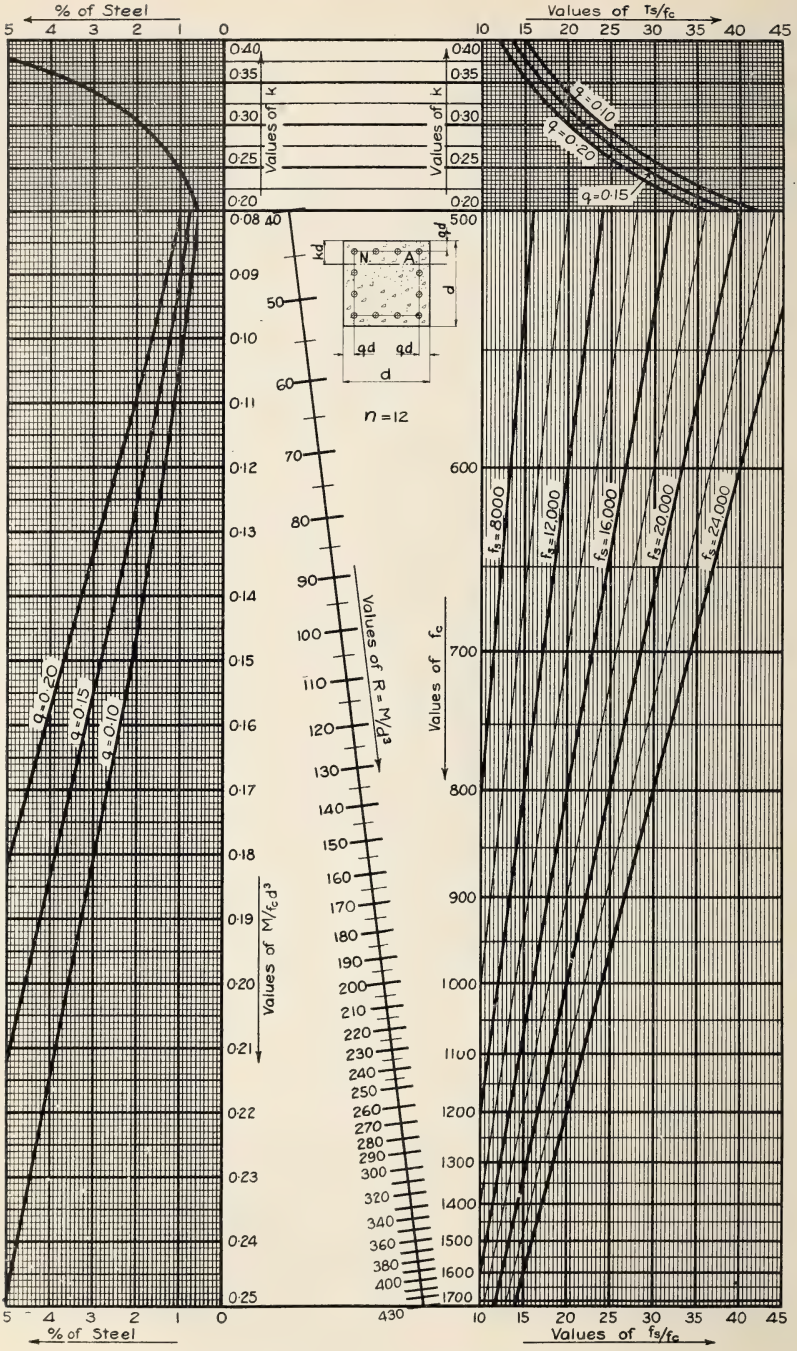


Fig. 3. Solid Square—Metal Girdle Assumed Continuous.

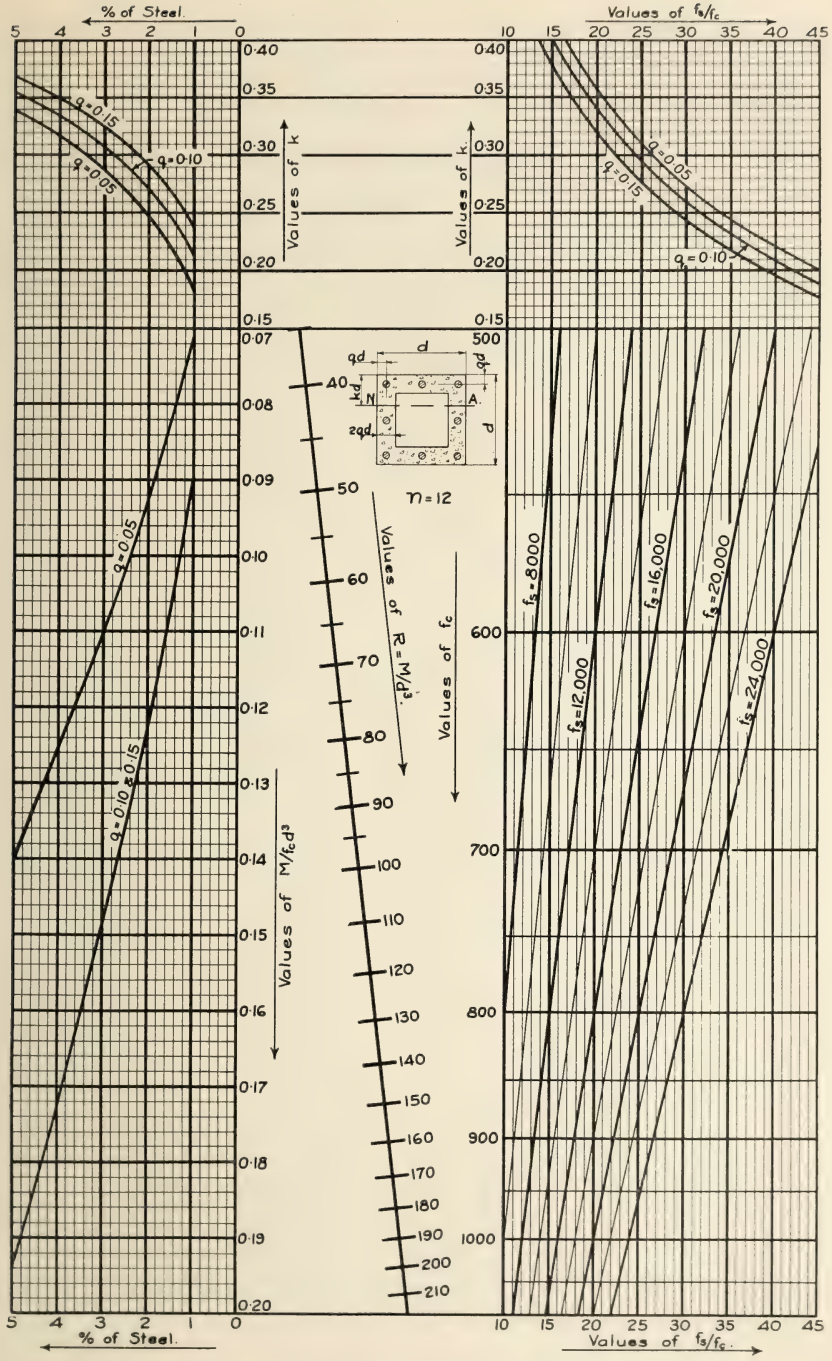


Fig. 4. Hollow Square—Eight Individual Rods.

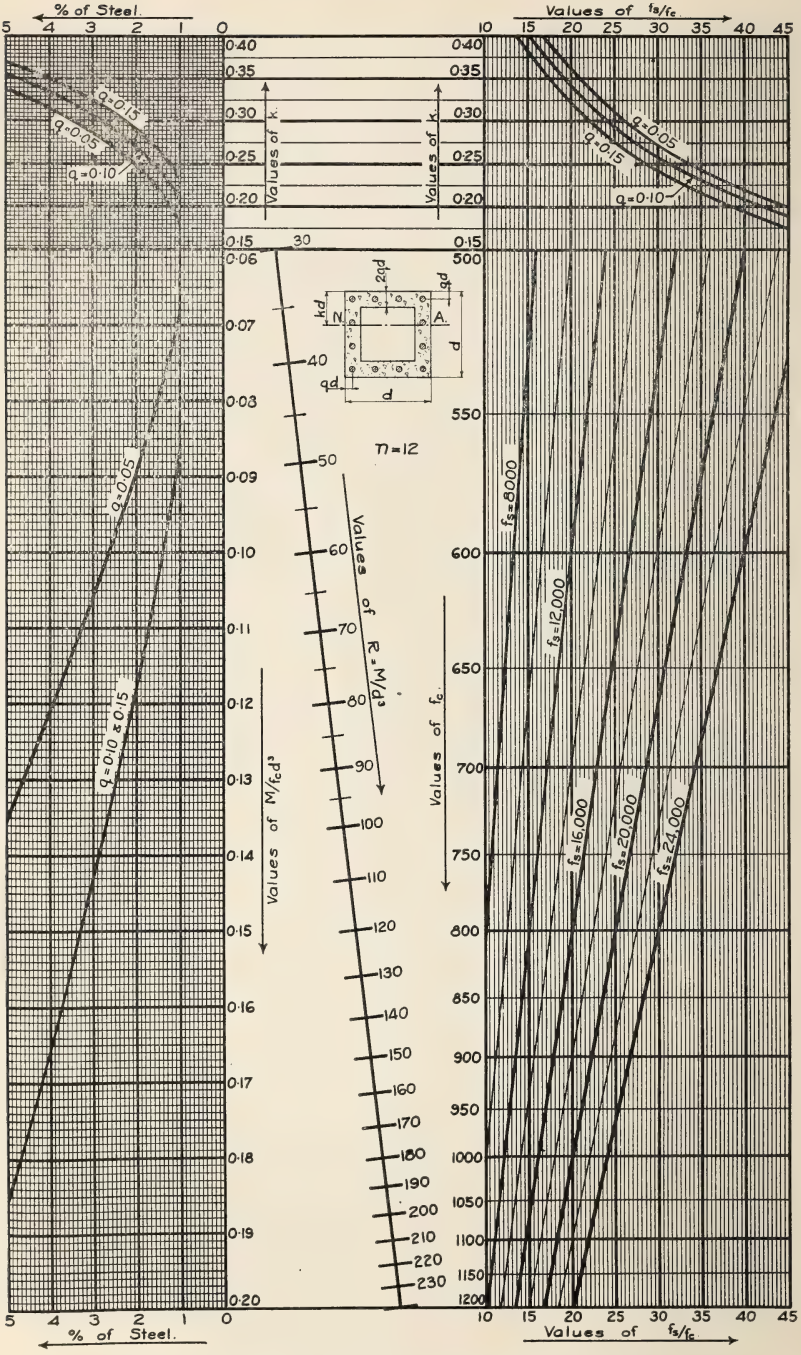


Fig. 5. Hollow Square—Metal Girdle Assumed Continuous.

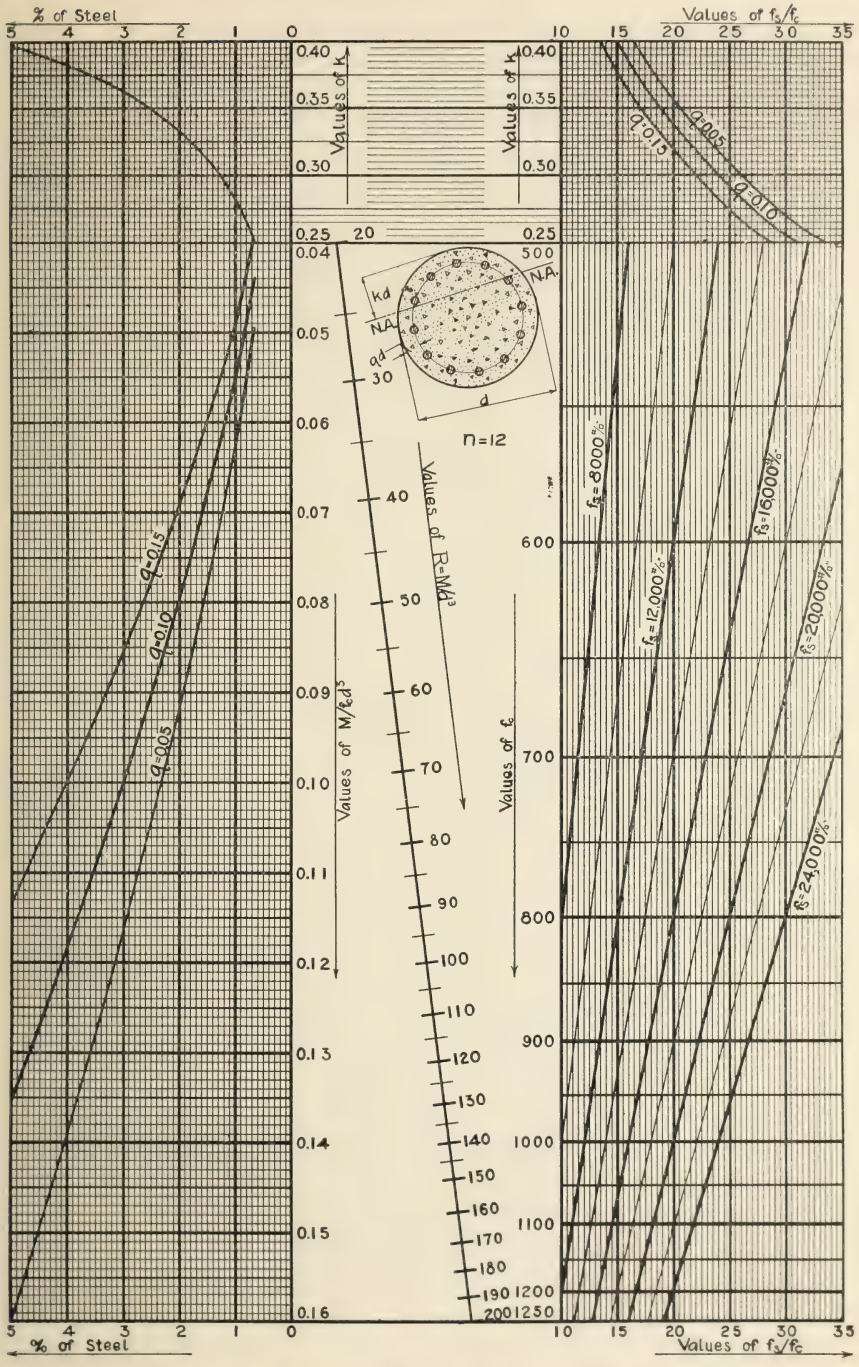


Fig. 6. Solid Circle—Metal Girdle Assumed Continuous.

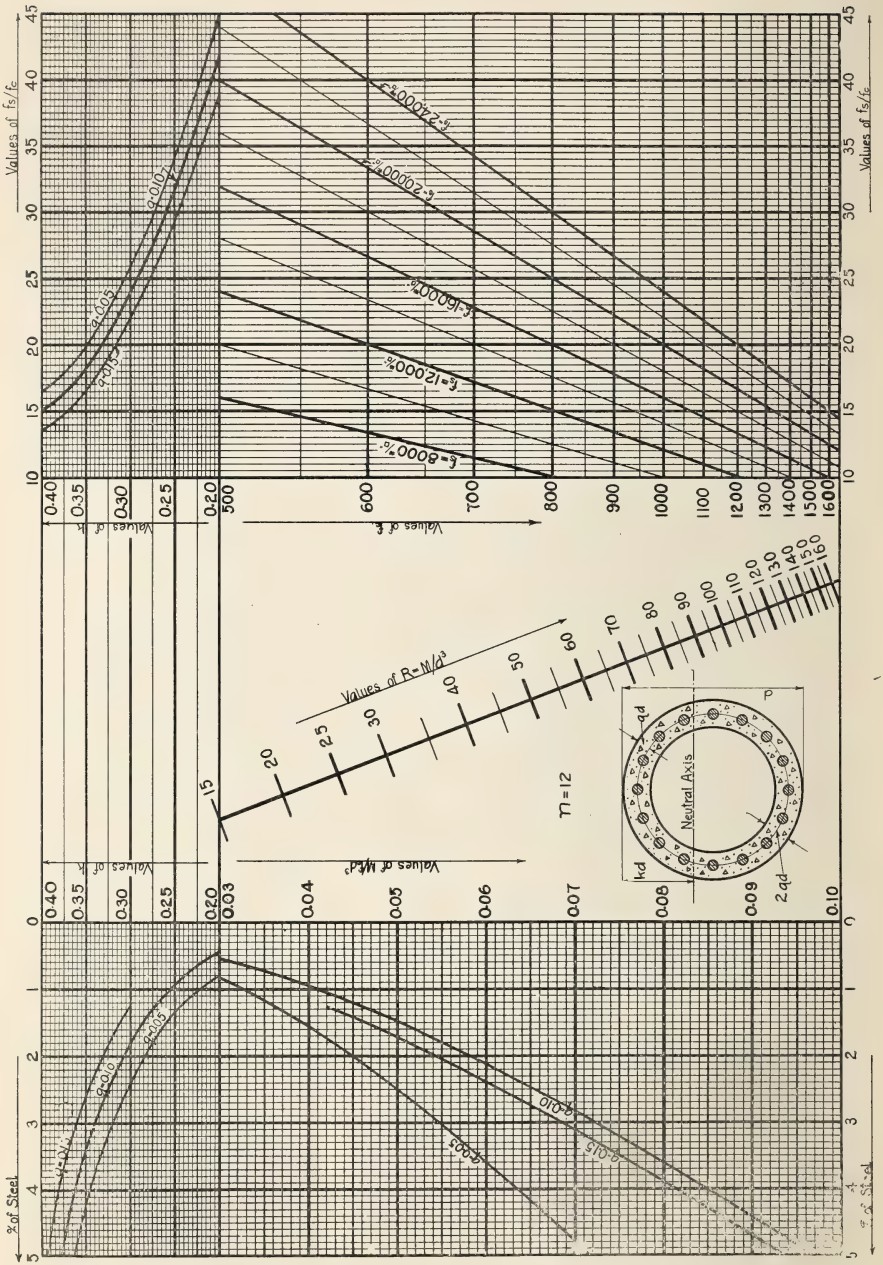


Fig. 7. Hollow Circle—Metal Girdle Assumed Continuous.

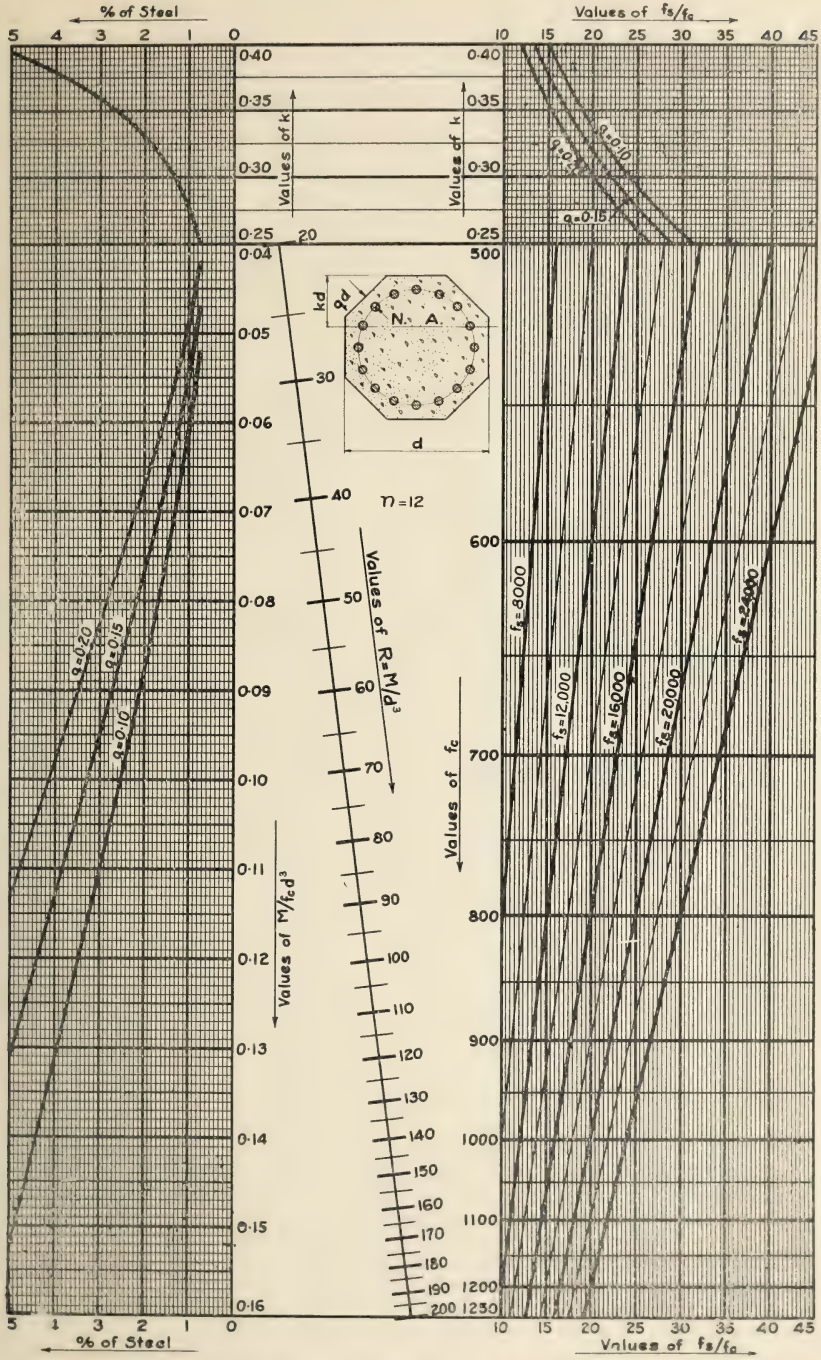


Fig. 8. Solid Octagon—Metal Girdle Assumed Continuous.

hand corner of the figure was constructed. The right hand side of the diagram is practically the same for all pole sections and enables the user to select that pair of co-existent stresses which in his opinion, the character of his materials warrants. A value of 12 for n was assumed.

For other cross-sections, a somewhat analogous method was pursued. Many of the analytical solutions were checked by graphical methods.

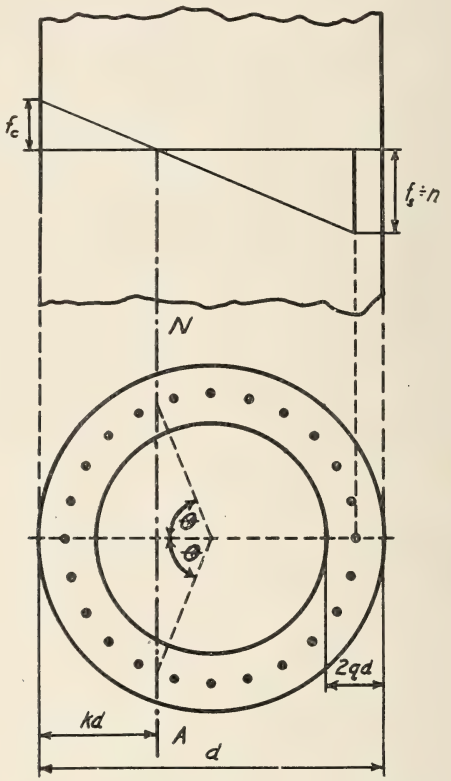


Fig. 9. Stress Distribution at Cross-Section.

How to Use the Diagrams

Usually, though not always, the starting point will be the point on the percentage axis corresponding to the p for the pole in question. Keeping in mind always, the proper value of q, the upper left and lower left hand groups of curves give k and $M/f_c d^3$ values respectively until the point X, Fig. 10, is reached. Moving to the upper right, a value of f_s/f_c is found. The lower right hand group permits the user to select his stresses. For example, if f_s/f_c is 20, numberless combinations of

stress are available, of which 12,000 and 600, 16,000 and 800, 20,000 and 1,000 are a few. Having found f_c (at point Y) a straight edge between X and Y gives at Z, the correct value of R on the oblique line. The point to be remembered is that to locate X and Y, a continuous path through points a, f, c and g, having regard to the proper value of q and the stresses suitable to the occasion, must be followed.

To determine M, an alignment diagram, Fig. 11, has been constructed. This is simply a device whereby with a straight edge, the value of M or Rd^3 may be read off from the central ordinate in the figure for known values of R and d. Following are the solutions of a number of typical problems.

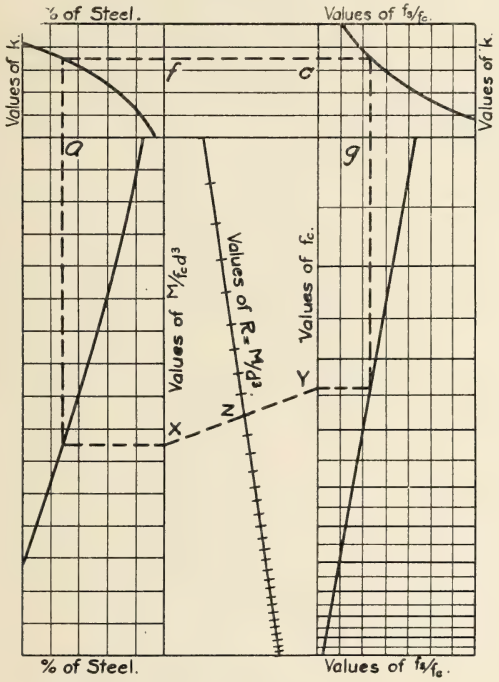


Fig. 10. Key Diagram.

PROBLEMS ILLUSTRATING THE USE OF THE CHARTS

Problem 1

Determine the bending strength at ground line of a 12-inch solid square pole having four reinforcing rods, the percentage of steel being 2, and q being .10. Safe stresses in steel and concrete may be taken as 16,000 and 800 respectively.

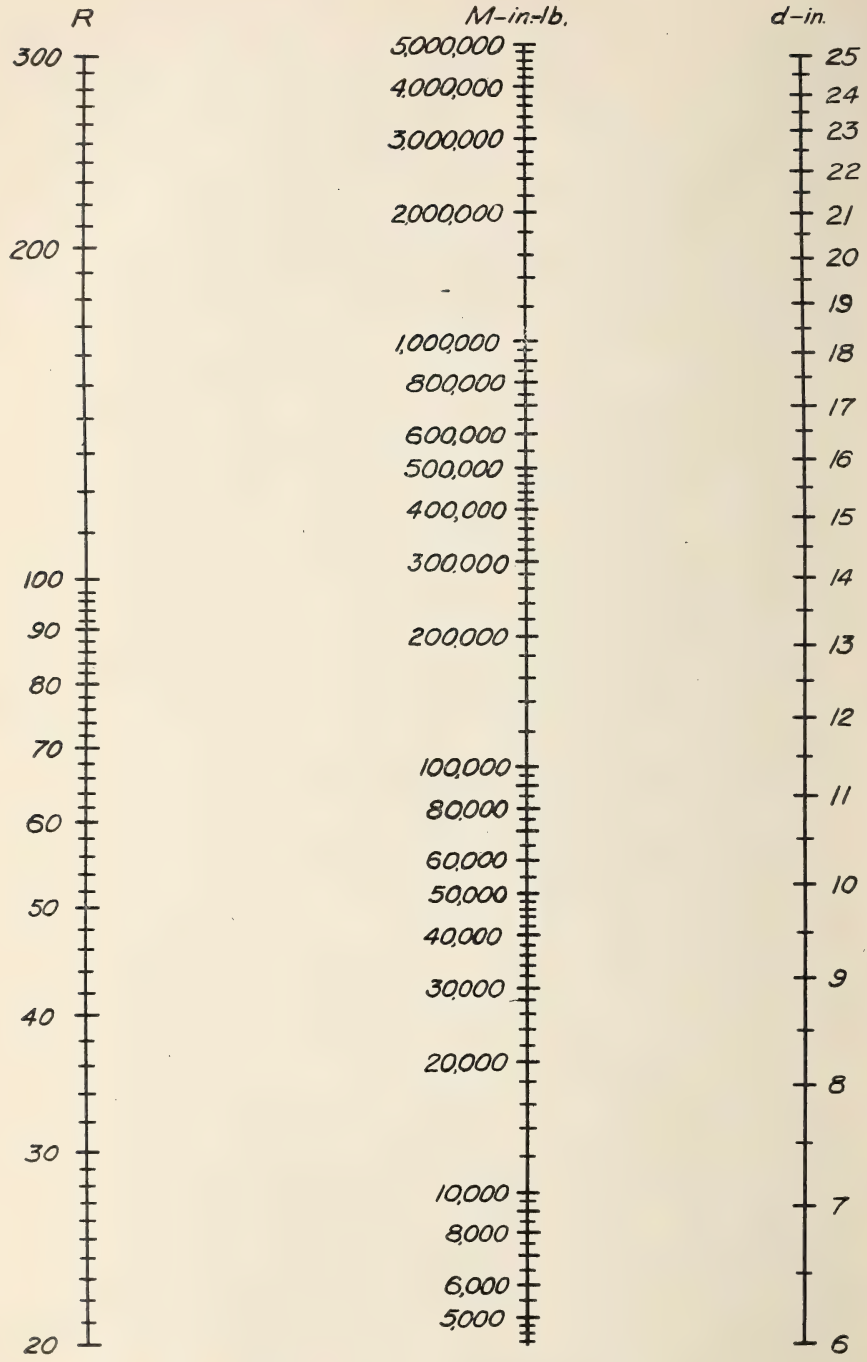


Fig. 11. Alignment Diagram for M.

Solution

Starting at the left, Fig, 1, with percentage equals 2 and remembering that $q = .10$, $M/f_c d^3$ is found to be .186 and k to be .305,

Proceeding thence to the right and downward f_s/f_c is seen to be 23, and 16,000 and 695 to be the necessary co-existent stresses. (The specified stresses cannot be realized simultaneously because the pole is under-reinforced.)

Joining with a straight edge .186 on the left with 695 on the right, R is found to be 129, Hence $M = 129 \times 12^3 = 223{,}000$ in.-lb.

If the pole be 40 ft, high, it will be good for a top pull of

$$\frac{223{,}000}{40 \times 12} = 465 \text{ lb.}$$

Problem 2

Determine the necessary percentage of metal in a solid round reinforced pole having $q = .10$, in order that 12,000 and 600 as stresses may exist in steel and concrete respectively at the same time.

Solution

In this case $f_s/f_c = 20$, Following to the left, Fig, 6, from the intersection of $q = .10$ with $f_s/f_c = 20$, k is found to be .336 and the percentage of metal to be 2.1.

It also follows that other simultaneous stresses in steel and concrete will be

8,000 and 400
10,000 and 500, etc., etc.

Problem 3

A solid octagonal pole 30 ft. high, q being .15, is to be designed to withstand a top pull of 1000 lb. Specified stresses are 20,000 and 1,000 respectively.

Solution

Here $M = 360 \times 1000 = 360{,}000$ in.-lb. From diagram Fig. 8, since $f_s f_c = 20$, k, by following to the left, is .318 and the necessary percentage of metal is 1.7.

Proceeding downward on the left to the $q = .15$ line, $M f_c d^3$ is found to be .071.

The straight edge joining .071 on the left with 1000 on the right gives $R = 71$.

Since $M = Rd^3$,

$$d^3 = M/R = \frac{360{,}000}{71} = 5070$$

and $d = \sqrt[3]{5070} = 17.9$ in. overall.

As an alternative, had the percentage of metal been 4, and had q been .10, a much smaller section would have answered. In that case,

$$k = .38$$
$$M/f_c d^3 = .131$$

But in that case f_c and f_s would be 1000 and 16,500 respectively.

The straight edge joining .131 on left with 1000 on right gives $R = 131$.

Then as before $d^3 = \frac{360{,}000}{131} = 2740$.

and $d = \sqrt[3]{2740} = 14$ in. overall.

This, though a smaller pole, is over-reinforced, which circumstance prevents the two specified stresses from occurring at the same time.

Other types of problem will suggest themselves to the user.

It will be observed that in some cases, the value of $M/f_c d^3$ is apparently a maximum for one particular value of q and that for all others, it is less. In the case of the hollow cylindrical pole, this is true, the value of $M/f_c d^3$ being generally less for $q = .15$ or $q = .05$ than it is for $q = .10$. In Fig. 12 a part of the information shown in the lower left hand corner of diagram Fig. 7, is amplified and presented in another form. The axes are p and q and the values of $Q = M/f_c d^3$ are plotted as contours. A glance at this diagram will show for example, that p being .05, $Q = .09$ when q is either .08 or .165, and that Q is a maximum when $q = .11$. Roughly speaking, Q for all values of p, is a maximum when q is .10 or .11 depending on the value of p.

The peculiarity just noted should be kept in mind when interpolating for values of $M/f_c d^3$. In two cases (hollow square sections), the values of $M/f_c d^3$ for $q = .10$ and $q = .15$ were so nearly identical that they almost coincided when plotted. One curve only of these two values of q has therefore been shown on these two diagrams.

DEFLECTION OF TAPERED POLES

For beams of constant cross-section,

$$\frac{dy}{dx} = \frac{1}{EI}\int M dx.$$

If, however, I be not constant, this becomes

$$\frac{dy}{dx} = \frac{1}{E}\int \frac{M}{I}\, dx.$$

Where I and M can both be expressed as simple algebraic functions of

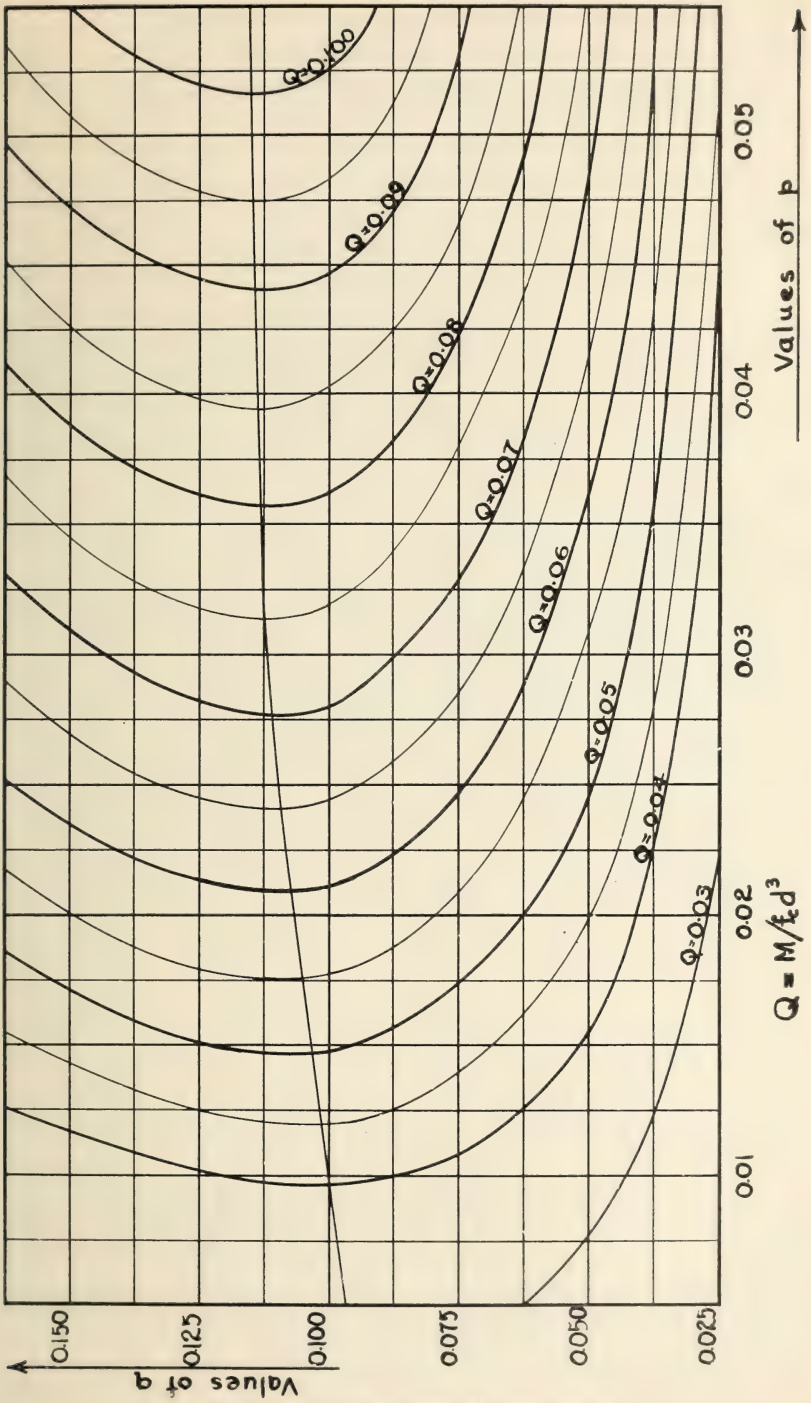


Fig. 12. Diagram Showing Variations in Q.

x, analytical methods are employed. When they vary in an irregular manner, graphical methods may be used.

For the cantilever shown in Fig. 13, the diameter at a section distant x from the support is

$$\frac{D}{l}\left\{l-x(1-t)\right\}$$

and if I_o represent the moment of inertia at the support, the moment of inertia at a section distant x therefrom will be

$$\frac{I_o}{l^4}\left\{l-x(1-t)\right\}^4$$

At this section, since W is an end load,

$$M=W(l-x).$$

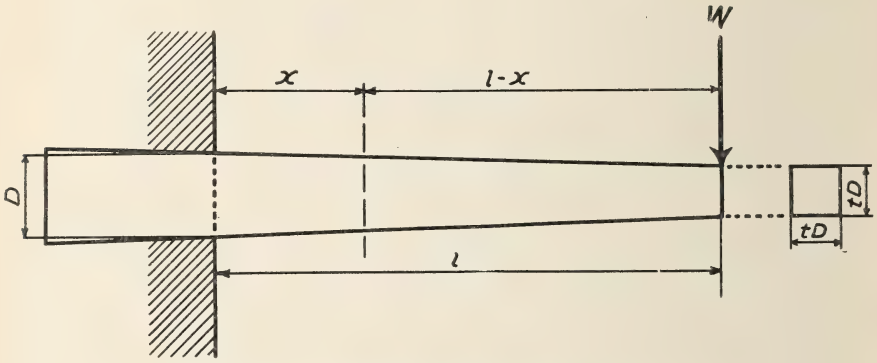


Fig. 13. Tapered Cantilever—End Load.

Substituting,

$$\frac{dy}{dx}=\frac{1}{E}\int\frac{W(l-x)l^4}{I_o\left\{l-x(1-t)\right\}^4}$$

Integrating, substituting and clarifying,

$$\Delta_1=\frac{Wl^3}{3tEI_o}$$

where Δ_1 is end deflection.

This equation shows that the end deflection of a tapered pole with end load is the deflection of a corresponding constant section pole divided by the taper ratio t.

Deflection formulas for homogeneous beams can be made applicable to reinforced concrete beams. The metal must be weighted of course to obtain its "equivalent" of concrete. The moment of inertia will take this weighting into account and also the fact that the integrity of the concrete has not been maintained past the reinforcement on the tension side. It will therefore be figured from the intact composite section as about the neutral axis. Interpreted in this way, the formulas

will give results approximating the actual performance of the beams. Strictly speaking, the only tapered reinforced concrete section to which the above formula for deflection will apply is a tapered pole of "constant quality". By this is meant one at all sections of which, the relative amount of reinforcement is constant, the position of the metal with respect to the section being constant also.

A tapered reinforced concrete pole, Fig. 14, having a base 5.46 in. square with rods placed 1/7 of the diameter in from the sides, was made

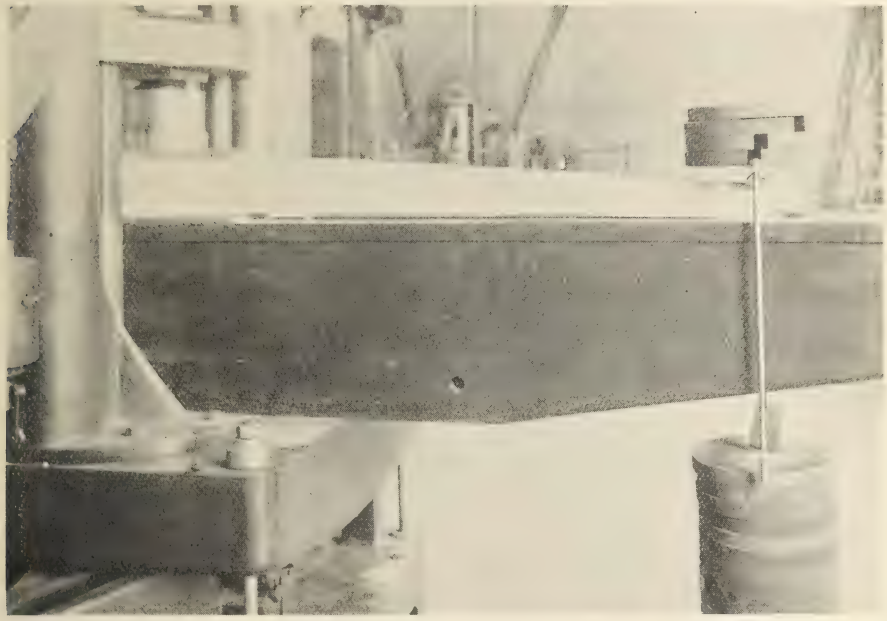


Fig. 14. Tapered Test Pole.

and tested for deflection. The reinforcement was $3\frac{1}{2}\%$ of the cross-section and consisted of four square rods. These were tapered in a milling machine so that at the outer end of the pole, where the outside dimensions were half those at the base, the rods had but half their original dimensions. Here also, the metal was placed 1 7 of the diameter in from each side. The pole was therefore one of "constant quality". The point of loading was 3 ft. 11 in. from the base at which point t, the taper coefficient, was .55. Young's modulus for the concrete was found experimentally to be 3,500,000 lb. per sq. in. and n was therefore taken as 8.5. The value of k computed from the formula

$$k = \frac{-pn - 1 - q^2 + 2q}{-2pn - 2 + 2q}$$

was .445. The base cross-section is shown in Fig. 15, the compression face being downward. Assuming the concrete intact except on the tension side outside of the plane of the metal, the moment of inertia I_o, of the base cross-section about the neutral axis, was found to be 80.8 in.^{4}.

$$I_o = 1/3\{5.46\ (.445\times5.46)^3+5.46\ (.412\times5.46)^3\}+8.5\times .52\{(.302\times5.46)^2+(.412\times5.46)^2\}$$
$$=46.6+34.2=80.8 \text{ in.}^4$$

For a load of 300 lb., the figured deflection is

$$\Delta_1=\frac{300\times47^3}{3\times3{,}500{,}000\times80.8\times.55}=.067 \text{ in.}$$

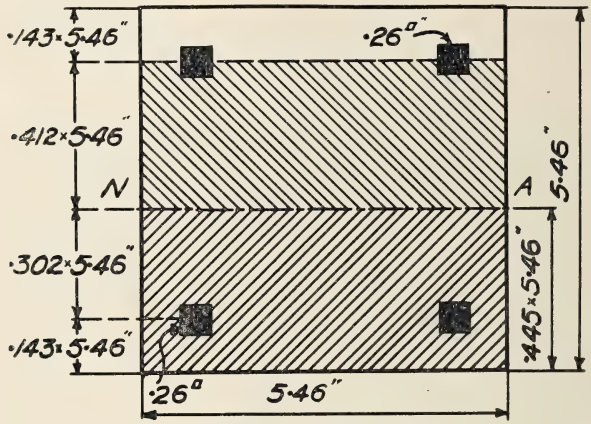


Fig. 15. Section at Base of Test Pole.

The following table gives a comparison between the actual and computed deflections up to a load of 300 lb. Failure took place at a load of 802 lb.

Load, lb.	Actual Deflection, in.	Computed Deflection, in.
30	.006	.007
60	.014	.013
90	.021	.020
120	.029	.027
150	.037	.034
180	.045	.040
210	.053	.047
240	.061	.054
270	.071	.060
300	.082	.067

In Fig. 16, the formula for the deflection of tapered poles has been charted to facilitate ready computation. The modular ratio, n, has

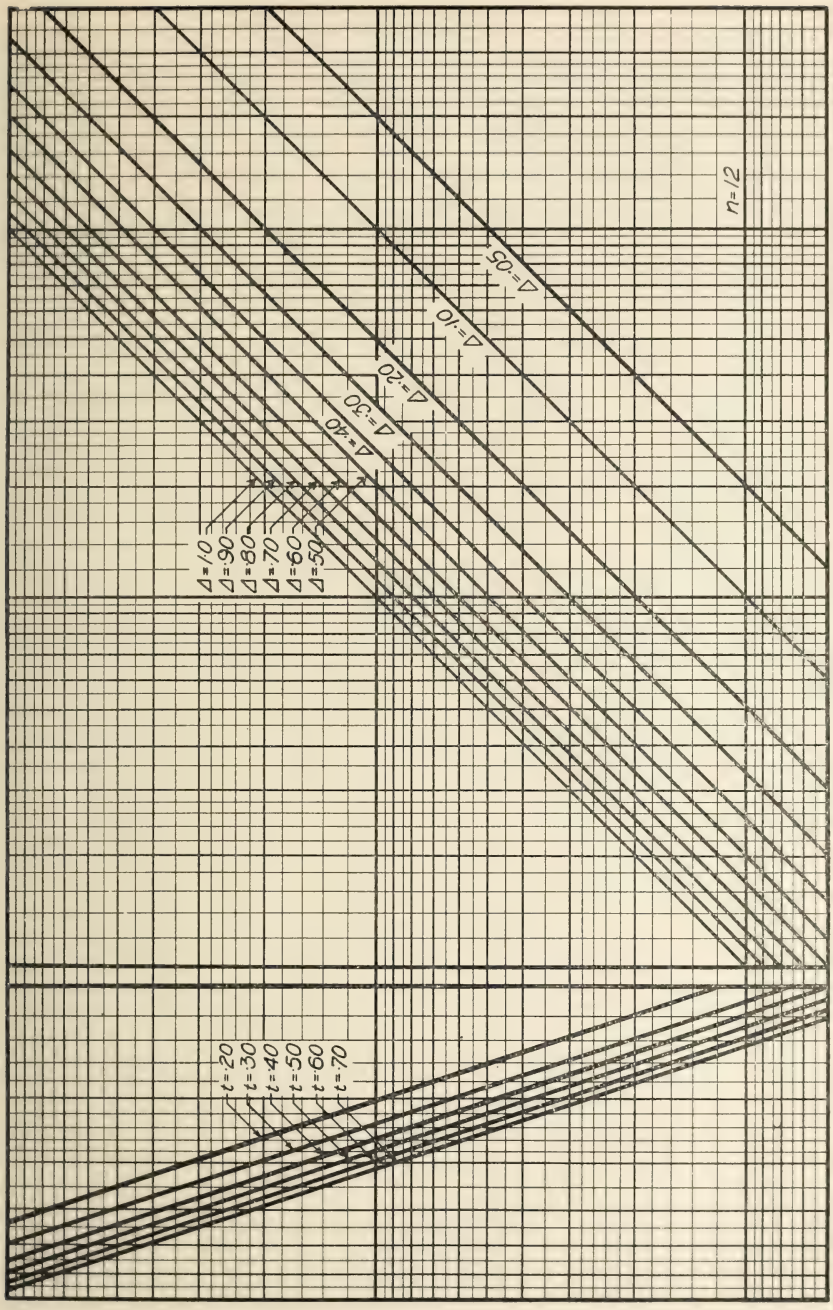


Fig. 16. Deflection Chart for End Loads.

been taken as 12. It should be remembered that in using the chart, Δ is the deflection for "constant quality" poles in inches per 100 lb. of top pull, l is free length in feet and I_o is in inch units. Suppose in a given case, W is 250 lb., l is 30 ft., t is .4 and I_o is 2000 in.^{4}.

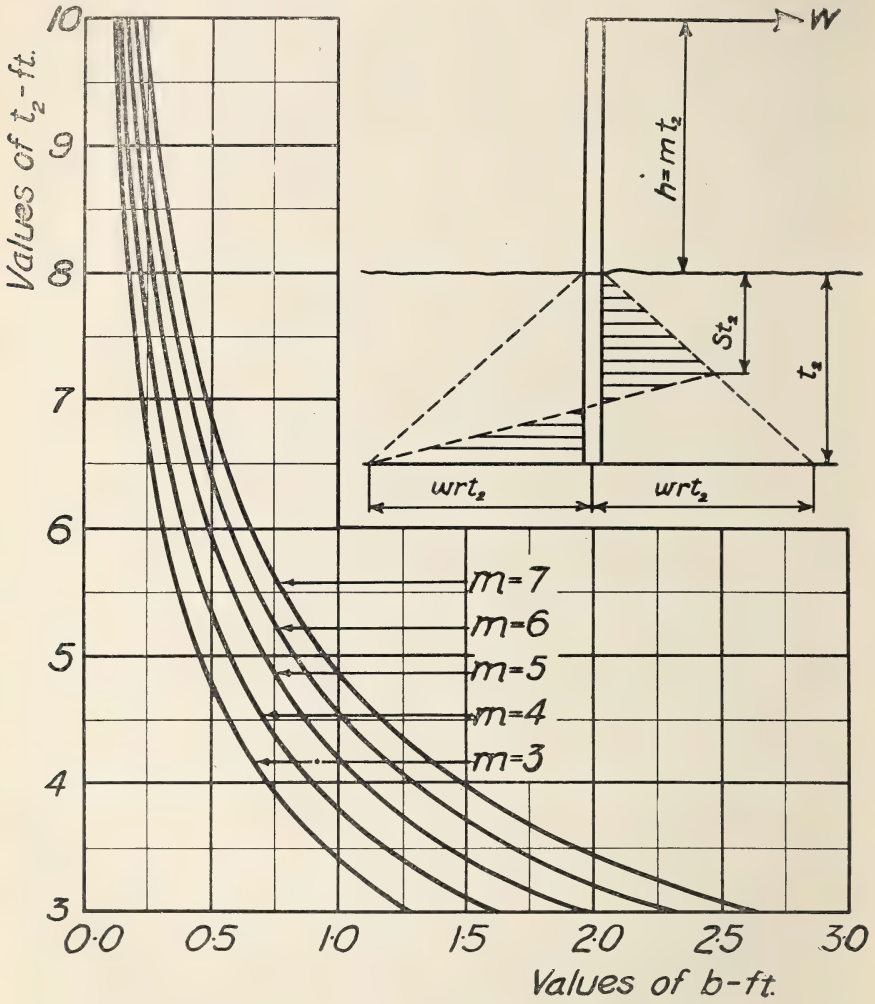


Fig. 17. Chart for Determining Underground Width.

Entering the diagram on the left where $l = 30$ ft. and proceeding upward to the $t = .4$ line, thence to the right, it is found that an intersection with the vertical from $I_o = 2000$, gives $\Delta = .8$ in. This then is the end deflection due to a top pull of 100 lb. For a load of 250 lb., the end deflection will be $.8 \times 2.5 = 2.0$ in.

In case an intersection lies outside of the parallel sloping lines, a modification of the method may be made. Where $l=40$ ft., $t=.5$, and $I_o=1000$ in.^{4}, it is found that the intersection on the right lies entirely above the sloping lines. Had I_o however, been 3000 in.^{4}, the deflection per 100 pounds of top pull would have been 1 in. Since deflections, other things being equal, are inversely proportional to moment of inertia, it follows that for the data assumed, the deflection will be 1.0×3 or 3 inches.

PERMISSIBLE PRESSURE OF SIDE OF POLE AGAINST EARTH

In the majority of cases, the lateral pressure exerted by a pole against earth when subjected to a capacity pull at its upper extremity, much exceeds that which the soil should be called upon to bear. In other words, poles would have to be widened considerably below ground in order that they might not exert excessive lateral pressures against earth when subjected to top pulls which, as poles, they are perfectly capable of resisting.

In Fig. 17 has been charted a formula established by Dr. Heinrich Dörr in "Die Standsicherheit der Masten und Wände in Erdreich", published in 1922. The formula

$$W=\frac{wbrt_2^2s}{2(3m+s+2)}$$

in which w is the weight of a cubic unit of earth, b is width of pole at ground line and

$$r=\frac{1+\sin\phi}{1-\sin\phi}$$

ϕ being the angle of repose for earth, is based on the belief that the maximum permissible lateral pressure against earth at any depth t_x, is t_xwr. This it will be observed is a corollary of Rankine's theory of earth pressures.

If the pound and the foot be the units of force and length respectively, if ϕ be 34° (corresponding to a slope of $1\frac{1}{2}$ horizontal to 1 vertical) if w be 110 lb. per cubic foot and if $s=.51$ (a representative value), the width of pole per hundred pounds of top pull is

$$b=\frac{11.75m+9.84}{3.88t_2^2}.$$

In the diagram, Fig. 17, the maximum permissible lateral pressures against the soil are indicated by ordinates to the sloping dotted lines. The shaded portions represent to scale, aggregate pressures against the

Fig. 18. Pole Made by Centrifugal Process. Height 77 ft. Courtesy of Dyckerhoff and Widmann, Dresden, Saxony.

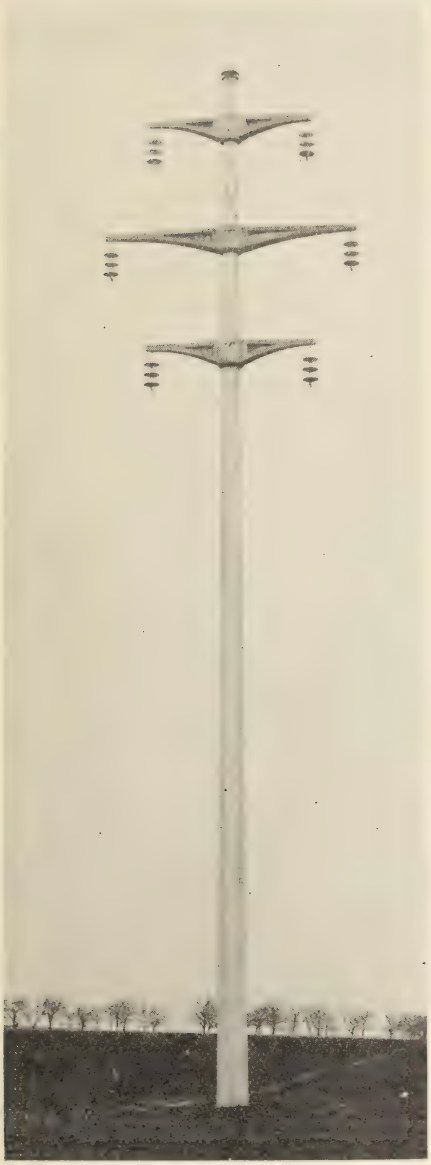


Fig. 19. Double Pole with Reinforced Concrete Cross-Arms. Height 65 ft. Courtesy of Dyckerhoff and Widmann, Dresden, Saxony.

earth, right and left, whose difference, obviously is W. The curves on the diagram give the width of pole per hundred pounds of top pull necessary in order that safe pressures be not exceeded. If for example, h be 30 ft. and t_2 be 5 ft., m is 6. Entering the chart at $t_2 = 5$ and proceeding to the $m = 6$ line, b is found to be .8 ft. This means that the width b, of the pole per 100 lb. of top pull should be .8 ft. at the ground line.

The writers wish to acknowledge with many thanks, the valuable assistance of Messrs. W. B. Dunbar and Karl Irwin in the preparation of certain of the drawings which have been reproduced here.

NET SECTIONS OF DRILLED PLATES

By C. R. Young, *Professor of Structural Engineering*,
and W. B. Dunbar, *Instructor in Engineering Drawing*

Some consideration of the true net section of riveted tension members from the theoretical point of view was given by C. R. Young in Bulletin No. 2 of the School of Engineering Research, University of Toronto. That study was based upon the usual hypothesis that the nature of the stress at any point on a diagonal section between rivet holes in a tension member is the same as the nature of the stress at any point on a right cross-section of a member subjected to pure bending. The determination of the maximum stress at any point on a diagonal section was consequently made by application of the formula for maximum resultant of the normal and the two tangential stresses at any point on a beam cross-section. Diagrams and an approximate rule for net section were prepared on the basis of this theory and were incorporated in the bulletin mentioned.

It is realized, however, that the state of stress on a diagonal section between two rivet holes in a tension member is not nearly so simple as the state of stress on a right section of a beam, although the latter may perhaps approximate the average condition tolerably well.The actual nature of the stress for the various practicable sizes of holes and stagger ratios is not known, but no doubt it is complicated. Investigation of the matter by the methods of photo-elasticity is now being carried on by Professor T. R. Loudon, of the University of Toronto, and doubtlessly the true variation of stress for typical cases will be shortly made known. In the meantime, however, it was thought well by the authors to carry out certain practical investigations along other lines, and to make such alterations in the diagrams already published in Bulletin No. 2 of the School of Engineering Research as will represent more closely the known resistance of a perforated tension member.

Tests on Rubber Models

In considering the most convenient way of disclosing the stress condition on a diagonal section of a perforated tension plate, it occurred to the authors that the use of rubber strips subjected to tension might be helpful. Consequently, rubber bands 6 by 1 8 in. and 6 by 3 16 in., 18 in. long, were prepared with two pairs of 13 16-in. holes placed at $2\frac{1}{2}$ in. stagger and 3 in. gauge, one set of holes being near the loaded end of the strip and the other set 7 in. farther from this end. Fig. 3

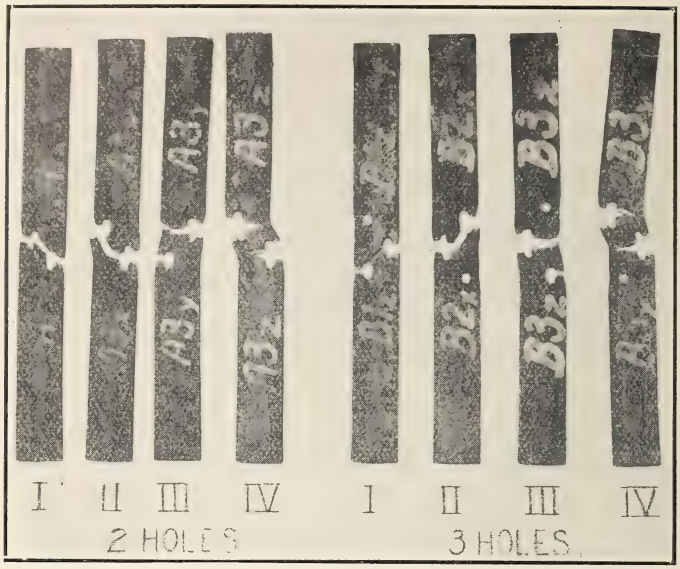


Fig. 1.—Typical Failures for 3½-in. Plates.

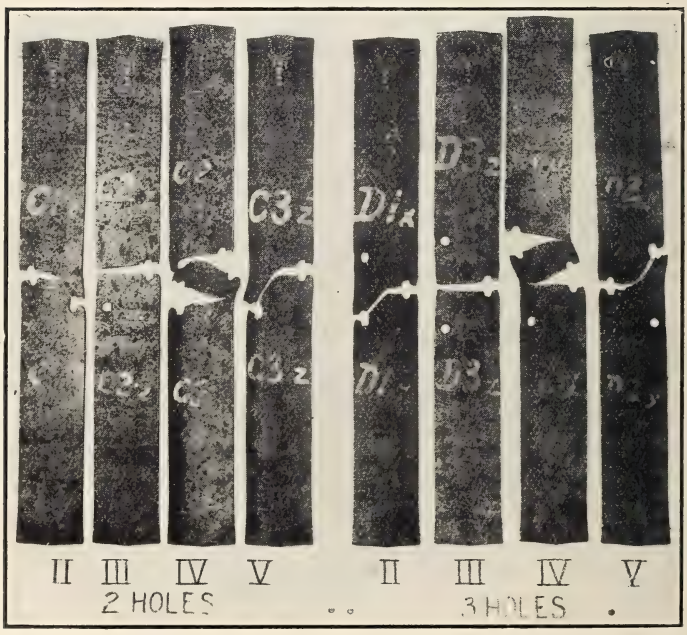


Fig. 2.—Typical Failures for 5¾-in. Plates.

indicates the relative location of the holes and their situation with respect to the edges of the rubber strips. This diagram refers in particular to the 6 by 3/16-in. strip, and what follows will apply specially to that model, although similar results were obtained earlier from the thinner strip.

The rubber was fixed at one end by clamps to a table and was loaded by means of tightly fitting brass pins at the two holes nearest the free end. A special device was arranged for applying load to these pins involving the passing of cords over pulleys with weighed quantities of shot suspended from the ends of the cords. In order to reduce friction to a minimum, the rubber and the loading devices were both supported clear of the table top by means of ¼-in. ball bearings between plates of glass. For each point whose movement was determined, an increment of loading of 100 grams was applied, until the maximum load reached 1,200 grams.

The displacement of a series of 13 points on each of the eight cross sections, *A-A*, *B-B*, *C-C*, etc., was determined by means of micrometer microscopes. The load was applied and after an interval of one minute the reading was taken. The process was necessarily exceedingly slow as the rubber recovered slowly after the removal of the load and only one point could be observed with a given position of the microscope.

The displacement of the various points observed is indicated in Fig. 3. Actual observed positions of the points, after certain representative loadings, for the eight cross-sections are indicated with black dots. It was a source of considerable surprise to find that the displacements of points on a given cross section were so nearly alike. There appeared to be a general uniform drag of the rubber in the direction of the load with nothing like so great a variation of point displacement along the cross-section as was anticipated. It was noted that points farthest to the right or left of the centre line of the strip tended to move slightly towards the centre at all of the sections. The unloaded or open holes had apparently no effect on the displacement of points adjacent thereto.

As a means of comparing the behaviour of points on the various cross-sections with those on a typical unperforated right section, the section *C-C* situated midway between the two pairs of holes was adopted as a standard and the maximum displacements of points on the other cross-sections that ought to occur by virtue of their greater or less distance from the clamps at the fixed end was plotted as shown by the hollow squares in Fig. 3. It is seen that the actual displacements are very much the same as should occur in an unperforated piece of rubber having regard to the distance of the section under consideration from the fixed support.

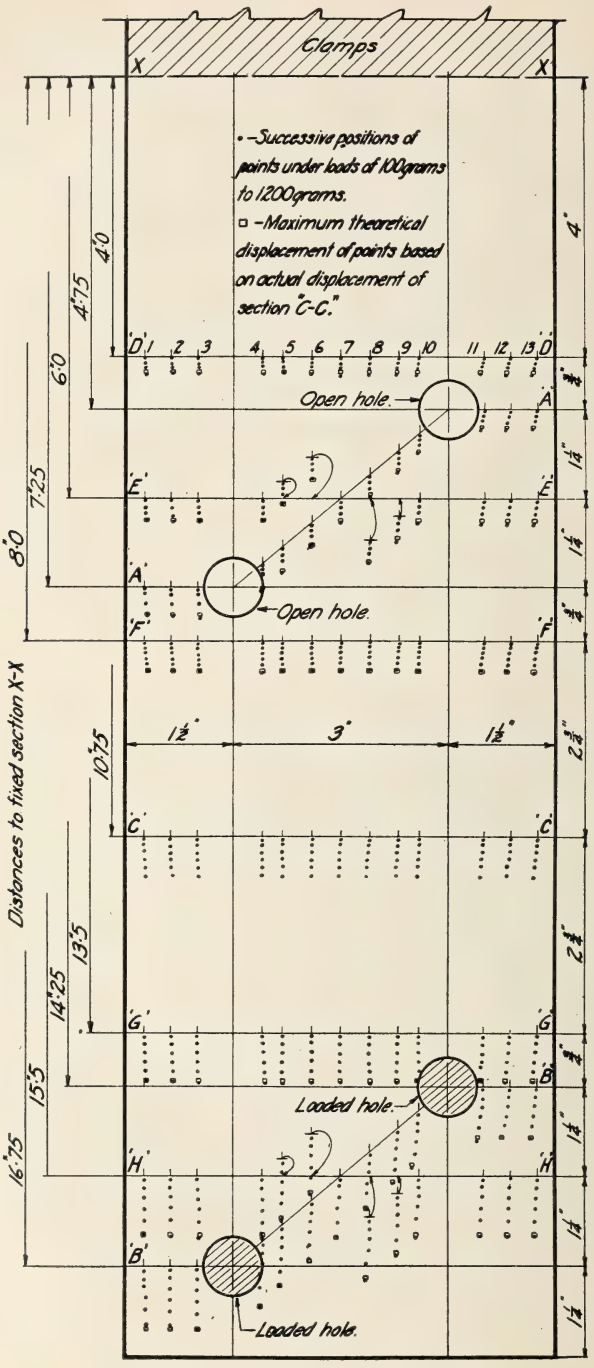


Fig. 3.—Movement of Points on 6×3/16-in. Rubber Band Loaded at Two End Holes.

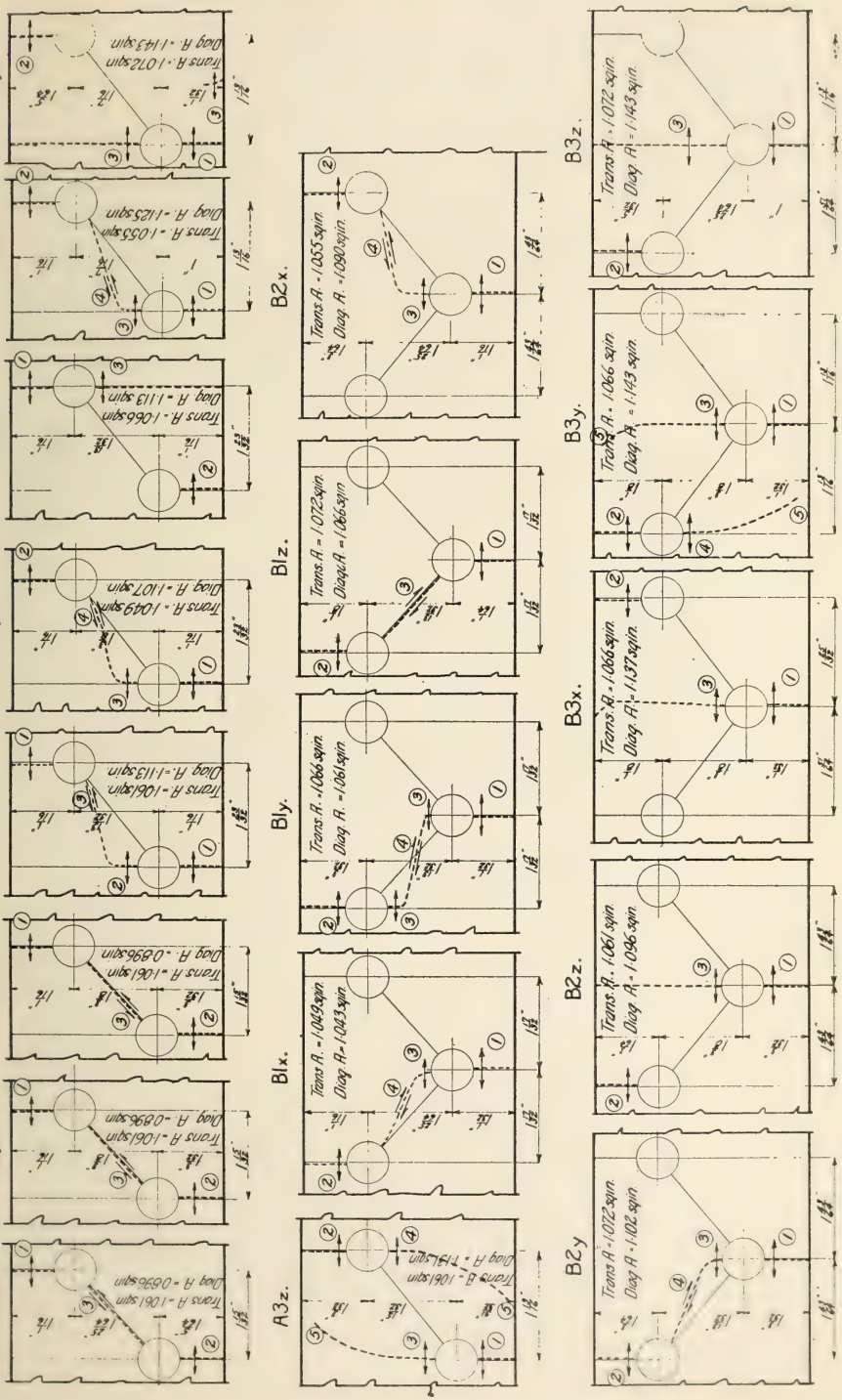


Fig. 4.—Failure of Individual Specimens, Series A and B (3½-in. Plates).
(See Fig. 7 for Explanation of Symbols).

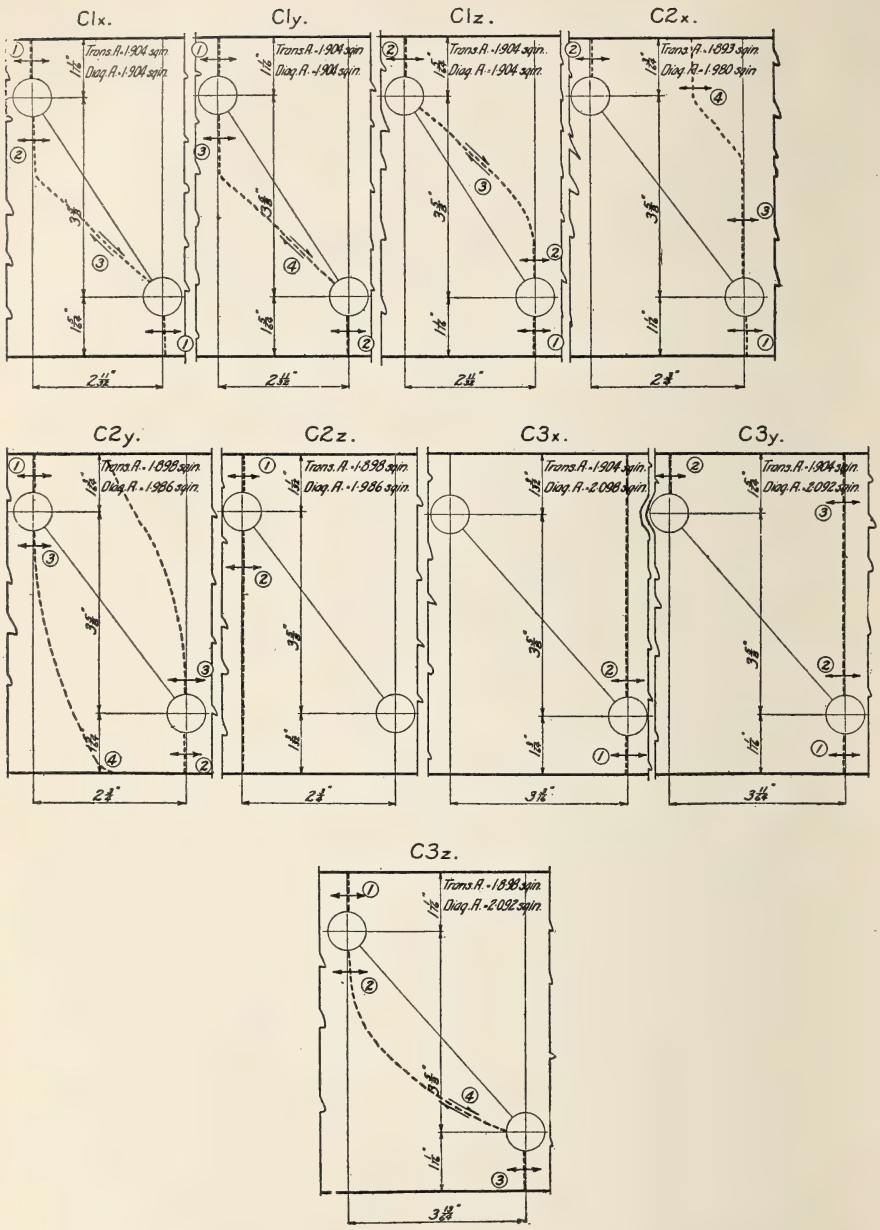


Fig. 5.—Failure of Individual Specimens, Series C (5¾-in. Plates).
(See Fig. 7 for Explanation of Symbols).

The results of this experiment were somewhat disappointing. It had been expected that a substantial variation in stress from point to point along a section in the neighbourhood of perforations would be evident. It cannot be said, however, that the models disclosed any pronounced variation of the kind anticipated. The recorded behaviour of steel tension specimens tested to destruction lead the authors to believe that there would be marked indication of high intensity of stress around the rivet holes, but little evidence of this kind was disclosed by the rubber models. There was, on the other hand, an indication of almost uniform stress on any given cross-section.

TESTS OF DRILLED PLATES

Since it appeared impossible to obtain accurate predictive information by the use of rubber models, it was decided to test to destruction a series of drilled steel plates with different widths and rivet arrangements. In all, thirty-six specimens were tested. Of these, eighteen were 3½ by 3/8 in., approximately, the remaining eighteen being 5¾ by 3/8 in., approximately.

Specimens 3½ in. wide were designated *A* where only two holes were used and *B* where three holes were used. Specimens 5¾ in. wide were correspondingly designated *C* and *D*. For all specimens the holes were drilled and were of 11/16-in. diameter. Three different stagger ratios were employed. All specimens designated with the figure "1" were designed with a stagger ratio such as to give equal diagonal and right cross-sectional areas. Specimens marked "2" were designed with a stagger ratio such as to give a diagonal area midway between that given by the specimens marked "1" and those marked "3". Specimens marked "3" were designed with a stagger ratio such as to give a diagonal area corresponding to a deduction of $x=0$ for the second hole, as given by the formula

$$x = \frac{g}{h} - \frac{2\left\{g^2+s^2-h(g^2+s^2)^{\frac{1}{2}}\right\}}{h\left\{g+(g^2+4s^2)^{\frac{1}{2}}\right\}}$$

The *X* specimens in all series were tested with open holes and the *Y* and *Z* specimens for all series were tested with holes plugged by inserting with a driving fit a turned cylindrical piece of steel.

Specimens marked *A* and *C* contained two holes only, three stagger ratios being provided, as already described. Specimens marked *B* and *D* all had three holes so arranged that the two staggers were equal, the stagger ratios corresponding respectively to those in the *A* and *C* groups; that is for specimens *B1X*, *B1Y* and *B1Z* the stagger ratio

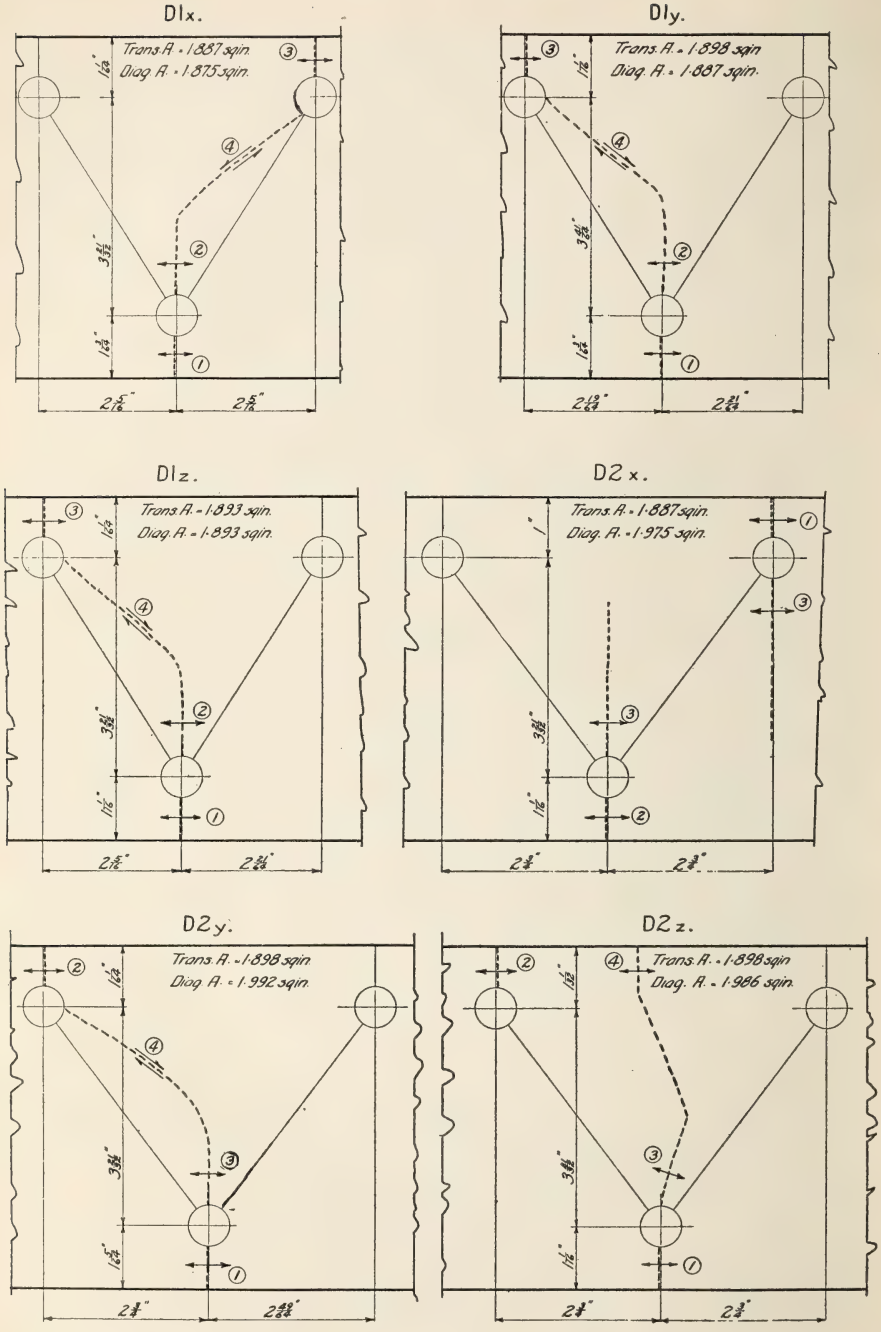


Fig. 6.—Failure of Individual Specimens, Series D1, D2 (5¾-in. Plates).
(See Fig. 7 for Explanation of Symbols).

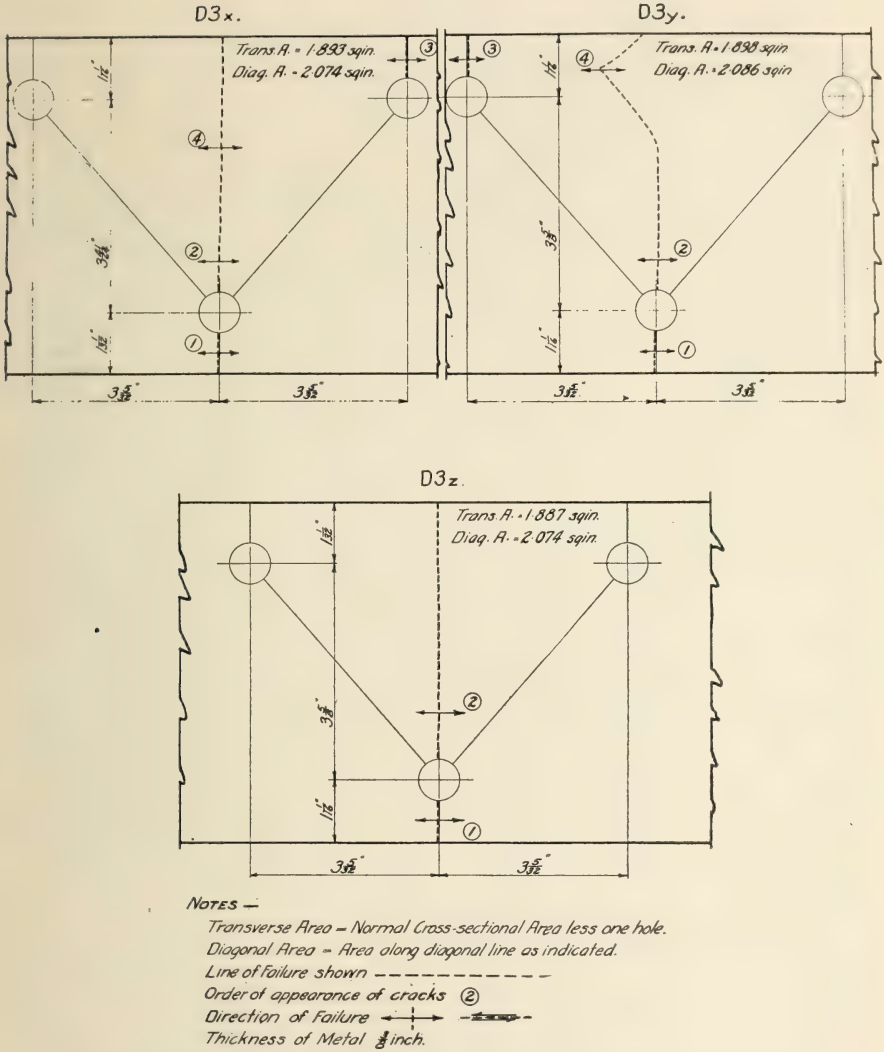


Fig. 7.—Failure of Individual Specimens, Series D3 (5¾-in. Plates).

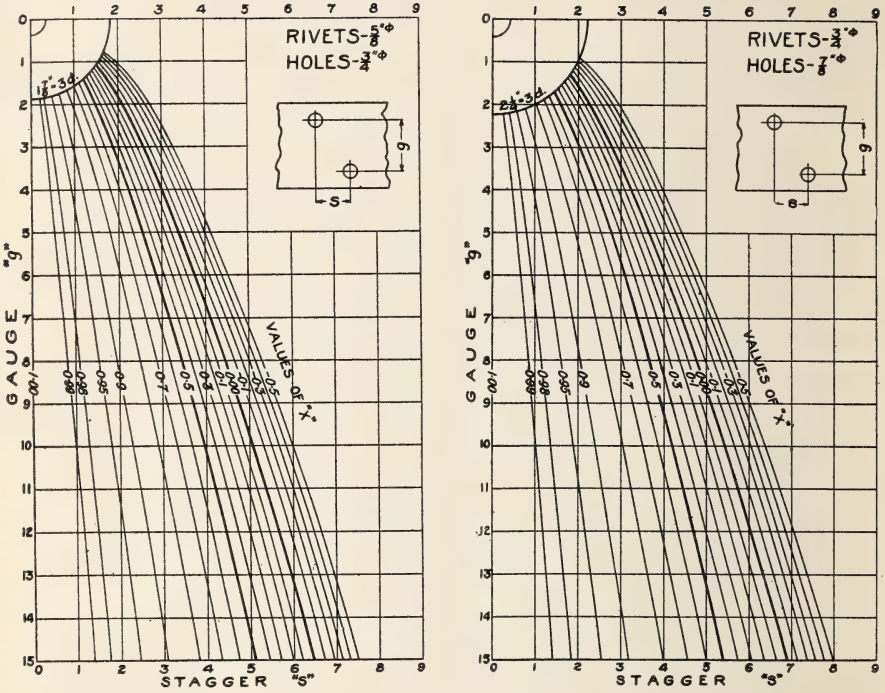


Fig. 8.—Deduction Diagram for 5/8-in. and 3/4-in. Rivets.

corresponded respectively to that for specimens *A1X*, *A1Y* and *A1Z*, stagger ratios for *B2X*, *B2Y*, and *B2Z* corresponded with those for the *A2* group; and stagger ratios for specimens *B3X*, *B3Y* and *B3Z* corresponded to those for the *A3* group, and so on. Specimens of *C* and *D* groups were strictly comparable, respectively, with those of *A* and *B* groups except that three holes were used instead of two, and a double opportunity for diagonal failure was consequently given.

The specimens were tested to destruction in a 200,000-lb. Riehlé testing machine. A careful record was made of the manner of failure of each of the specimens and this is given in detail in Figs. 4 to 7, inclusive. Characteristic or type failures are also shown in Figs. 1 and 2.

Observation of the specimens under load indicated, amongst other things, the following:

(1) Scaling always occurred along the line diagonally adjoining the centres of the holes.

(2) Thinning of the metal at the edges of the holes occurred under high stress with nicking at the holes and elongation thereof accompanied by realignment of the axis of the bar.

(3) Cracks always started at the outer edge of a hole first and progressed gradually towards the edge of the bar.

(4) Plugging of holes did not have any appreciable effect either on the line of the failure or on the ultimate loads. It, however, was observed that there was less tearing and a louder report at failure when the holes were plugged; that there was less thinning of the plate at the edges of the holes, less distortion of the holes under small loads and less tendency for the axis of the specimen to realign itself.

A study of Figs. 4 to 7, inclusive, will show clearly the point of initial failure and the manner of progress of failure in the case of each specimen. The particular method of designating these facts is indicated in the explanation of symbols given in Fig. 7. Thus, for example, the failure for specimen *A1X* occurred along the diagonal dotted line. The numbers in circles indicate that the initial failure occurred between a rivet hole and one edge of the plate, the second stage of failure took place between the opposite rivet hole and the near edge of the plate and the final stage was the shearing of the metal between the rivet holes.

ANALYSIS OF FAILURES

A study of the failures of the various specimens indicated in Figs. 4 to 7, inclusive, indicates that there are five different types of failure, conveniently grouped in Figs. 1 and 2. Fig. 1 applies to $3\frac{1}{2}$-in. plates

and Fig. 2 to 5¾-in. plates. For the narrow plates, the four classes of failure found for the 2-hole specimens are repeated for the 3-hole specimens. For the wider plates, type I failure, that is one involving a straight shear between rivet holes, did not occur. For these plates types II, III, IV and V are found both for the 2-hole and the 3-hole specimens. This would indicate that where the stagger ratio in the 3-hole specimens is the same as the stagger ratio for the 2-hole specimens, there is no difference in behaviour under test.

It was at first thought that it might be possible, with a knowledge of the strength of the metal in small specimens, to calculate the true reduction in right sectional area by reason of the drilling of the holes. However, the unavoidable variation of the material and slight differences in the pitting of the surfaces by rust, as well as small variations in workmanship beclouded comparisons when dealing with such small differences in stagger ratios and areas. Consequently, no clear law could be discerned on analyzing the tests on the basis of load carried.

However, it was manifest that useful information could be obtained by observing the tendencies to diagonal and right sectional failure exhibited by the specimens with different stagger ratios. If the results for all specimens marked "1", that is, those with equal diagonal and right sectional areas, be reviewed, it is found that in every one of the twelve cases failure occurred along a diagonal or zig-zag section. For those specimens marked "2", which had an intermediate stagger ratio between that for specimens marked "1" and "3", there were 7 failures along a right section and 5 failures on a zig-zag section. For specimens marked "3", for which the stagger ratio was arranged so that the deduction x for the second hole would be zero, according to the theory employed in the paper by C. R. Young in Bulletin No. 2 of the School of Engineering Research, the failure was on a right section for ten of the twelve specimens, and on a diagonal section for the other two.

It is clearly evident, therefore, that a specimen with equal diagonal and right cross sections is not equally strong on the two sections. There is a distinct and special weakness along the diagonal or zig-zag section, as has been generally believed by most structural engineers. Even when the stagger ratio is increased to the intermediate figure represented by the specimens marked "2", five out of the twelve specimens failed diagonally, thus showing that there is about as much tendency with this stagger ratio for failure to occur on one of the sections as on the other. If, however, the stagger ratio be increased to give full security of the diagonal section, in accordance with the theory formerly applied to the problem, it is seen that an unnecessary strength is given to the

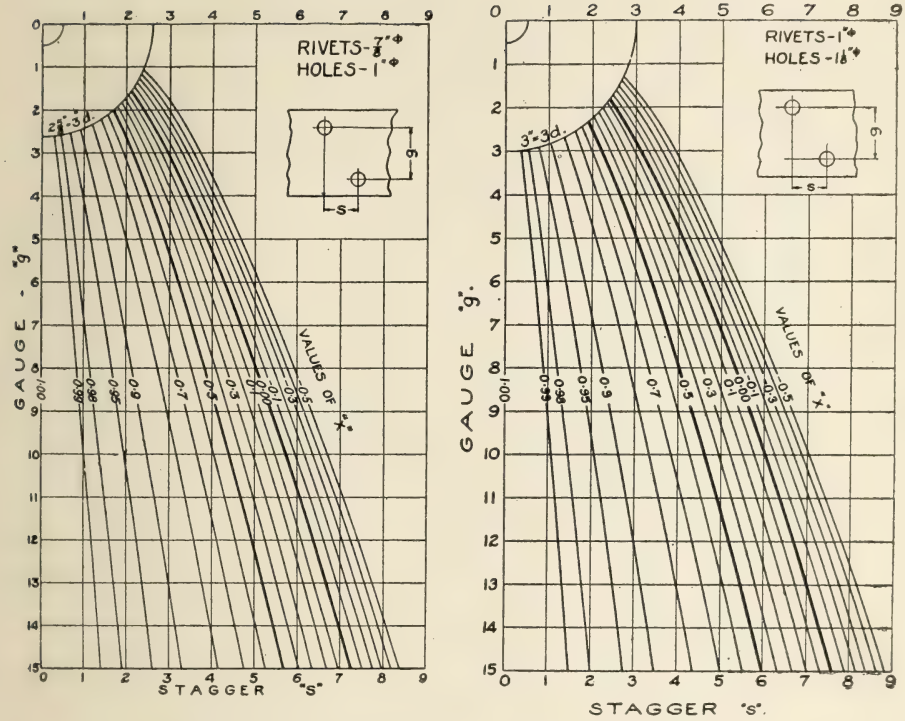


Fig. 9.—Deduction Diagram for 7/8-in. and 1-in. Rivets.

specimen, since only two out of twelve of the specimens failed diagonally, and these probably because of some special local difficulty.

In view of the fact that the theory employed in the former study was apparently somewhat too severe, it was thought well to modify the diagrams previously presented so as to make them less exacting. This has been done by fixing the position of the $x=0$ curve as intermediate between its position in the former diagrams and the position of the curve $x=0$ that would result from the plotting of the equal section formula $s=(2gh+h^2)^{\frac{1}{2}}$ given, for example, in the Carnegie Pocket Companion. The other curves were located with respect to the new $x=0$ curve so as to involve a proportionate shift from their former position. The resulting diagrams appear herewith as Figs. 8 and 9, a diagram for 1-in. rivets being now included in Fig. 9. In addition to lessening the severity of these diagrams, they have been extended by including negative values of x up to -0.5, so that in complicated sections the advantage of a large stagger ratio for any two successive rivets may be realized.

In cases where deduction diagrams are not available, it is helpful to have an approximate deduction rule which may be easily remembered. In Fig. 10 there have been plotted the deductions x for various stagger ratios as taken from the curves of Figs. 8 and 9. The approximate rule recommended for use where diagrams are not available is a rule proposed by Dr. D. B. Steinman which is $x=1.30-s/g$, where s is the stagger, g is gauge, and x in no case exceeds unity. This rule not only is very easy to remember, but it is most conveniently applied and gives results that are in nearly every instance on the safe side.

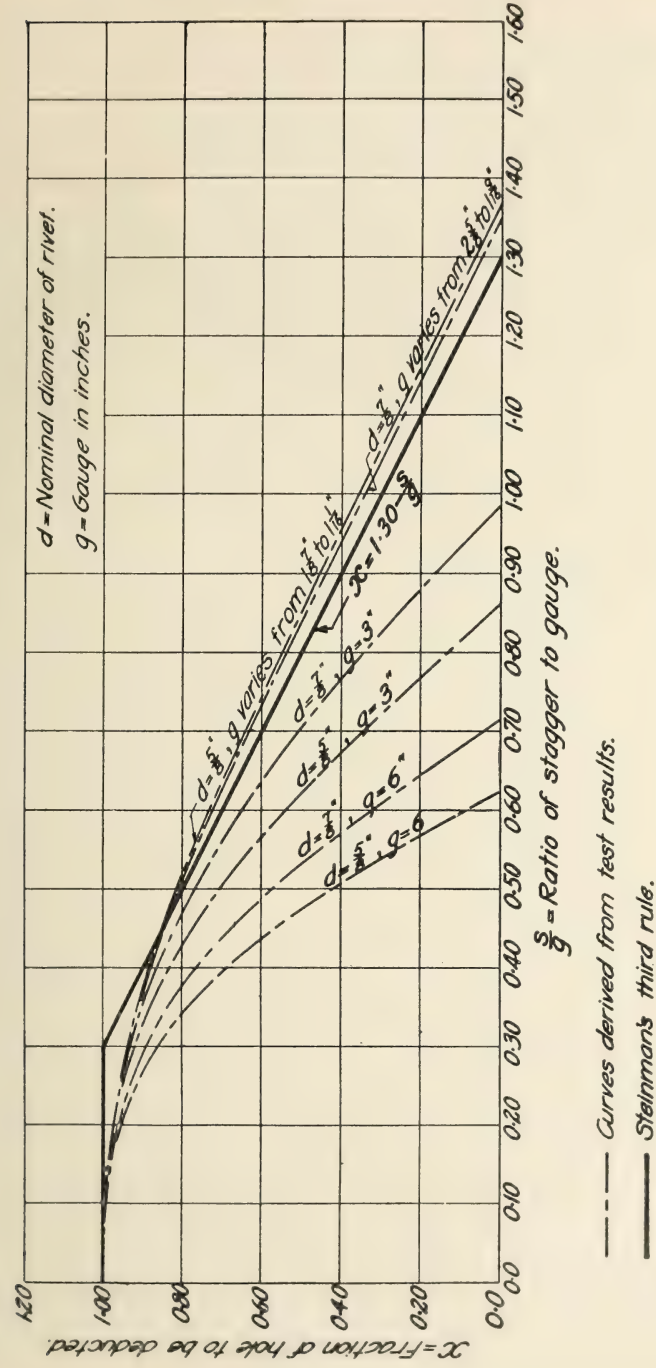


Fig. 10.—Basis of an Approximate Deduction Rule.

THE EFFECT OF HEAT UPON CELLULOSE

By J. W. Bain, *Professor of Chemical Engineering*,
and G. M. Chute, *Research Assistant*

In a previous paper[1] it was reported that cellulose when heated to about 200°C. was partially decomposed, yielding a number of non-volatile products which could be extracted by water. The significance of this observation lay in the fact that all previous investigators, including the senior author, had confined their attention to the volatile products obtained by heating cellulose, and the facts mentioned above were, therefore, quite unknown.

On continuing the investigation it became obvious that the various products formed must first be identified before any study of the varying conditions attending their production could be undertaken. For this reason, utilizing the results previously obtained, it was decided to select 200°C. as the temperature to which the cellulose should be heated, and the period was at least two hours at this temperature.

The apparatus which had been employed at first was small and unsatisfactory, particularly in respect to the measurement of temperature and the quantity treated. A large triple-walled electric oven, bearing a good reputation for uniformity in temperature distribution, was obtained, but when the cotton had been spread over the shelves the steady temperature varied from 235° on the lowest to 155° on the highest shelf. Interference with the circulation of the heated gases was no doubt responsible for this result.

A new rotating cylinder was then built, 24″ long and 10″ in diameter. It was heated on all sides by resistance wire strung along the inner walls of a box made of transite asbestos board, and a 1½″ layer of magnesia-asbestos cement was laid over the whole outside surface, except the ends. The rotating cylinder was carried on a ½″ pipe into which a thermometer could be slipped from one end, permitting the measurement of the temperature at the axis of the cylinder at about its centre. Three hours were required to raise the temperature to 200°, and the cotton was kept at this temperature for two hours.

When a considerable number of runs had been made in this apparatus it was found by chance that an automatically controlled electric furnace, made by Leeds and Northrup, was available. In this the temperature

[1]Trans. Roy. Soc. Can. [3], *18*, III, 269.

could be raised at a pre-determined rate to a definite point and there maintained;. the period chosen was two hours in rising from room temperature to 200°C. and three hours at this temperature. The cotton after heating was uniformly brown in colour, showing that the distribution of heat was satisfactory. The results of the heating in the two different forms of apparatus were so closely alike that no distinction could be made, and the temperature to which the cotton was subjected may be taken with considerable confidence as 200° ± 2°C.

Standard absorbent cotton extracted for seven days with hot distilled water was used as the raw material. After heating it was again extracted by boiling with water and the resulting solution was concentrated, decolorized with animal charcoal and obtained as a syrup, which was kept in a desiccator. The acidity was determined by titrating an aliquot with standard $Ba(OH)_2$ using the hydrogen ion apparatus to ascertain the endpoint.

The average yield of crude syrup from nine lots of cotton, each of 300 grams, was 3.36 grams per 100 grams of cotton. The average acidity corresponded to 6.5 cc. normal acid per 100 grams cotton.

The total loss in weight on heating was in one case 5.0%, while 2.45% of syrup was obtained. Hence, although the amount of syrup is small, it is a large fraction of the amount decomposed.

An attempt was then made to identify the substances present in the syrup.

An excess of $BaCO_3$ was added and after neutralization the insoluble residue was filtered off and reserved (A); the filtrate was concentrated and treated with an excess of alcohol to dissolve the saccharides and filtered; the residue (B) was set aside. The alcoholic filtrate was concentrated, decolorized with charcoal in aqueous solution, again concentrated and the treatment with alcohol repeated. The concentrated filtrate from this procedure was the purified syrup (C). The latter (C) was then examined as follows:

Pentoses and methyl pentoses were absent on the evidence of the usual colour reactions.

A sample was fermented with Saccharomyces cerevisiae, obtained from the Department of Zymology, University of Toronto; a blank and a solution of glucose were treated concurrently. There was a definite evolution of CO_2 indicating the presence of a hexose.

A portion of the syrup yielded a phenyl osazone, m.p. in Roth's apparatus, 210°; when mixed with an equal weight of phenyl glucosazone prepared from pure glucose, the mixture had an m.p. of 210°.

The p-nitrophenylosazone was prepared and had an m.p. of 255°.

No hydrazone could be obtained by the action of phenylhydrazine which would make the presence of mannose doubtful.

An attempt was made to obtain alpha-methylphenylosazone and o-nitrophenylydrazone, but neither of these could be prepared and identified. Accordingly the presumption is that fructose is either absent or is present only in very small quantity.

To determine the optical activity 1.75 g. syrup were dissolved in 7.00 g. water (solution d. = 1.07) and observed in a 1 dcm. tube; this gave +0.85° from which $(\alpha)_D^{20} = 3.97°$. Assuming that no other optically active substance is present in the syrup this would indicate the existence of 7.5% glucose.

When treated with Fehling's solution 0.500 g. syrup gave an average of 0.134 g. copper which would correspond to 13.6% reducing sugars calculated as glucose.

A sample of the heated cotton when removed from the oven was extracted in glass apparatus with distilled water. To the extract was added Na_2CO_3 to slight alkalinity and the solution was evaporated to dryness. Distillation with syrupy phosphoric acid yielded several fractions boiling from 95° to 110°; on concentration by freezing, formic acid boiling at 104.5° was obtained. The density of the solution was found to be 1.125, which corresponds to approximately 52% formic acid; the amount was 0.8 g. which was obtained from 200 g. of cotton. The amount of formic acid produced was therefore approximately 0.2% of the dry cotton taken.

Acetic acid is probably present also, but in very small amount; it could not be separated. No other acid appears to be present in the heated cotton.

The residues (A) and (B) referred to above have not been investigated, but this will be carried on at the first opportunity. A crystalline substance which separated from the residue (B) has not yet been identified.

In conclusion it may be stated that the presence of glucose in heated cotton as reported last year has been definitely established. Pentoses and methyl pentoses are apparently absent and the presence of hexoses other than glucose is very doubtful. Formic acid is produced in the heating and probably small amounts of acetic acid. No attempt has been made as yet to study the volatile products formed during the heating, and this will be taken up next.

AN INVESTIGATION OF SOME PROPERTIES OF PHENYLHYDRAZINE AND FACTORS AFFECTING HYDRAZONE FORMATION

By E. G. R. Ardagh, *Associate Professor of Chemical Engineering*, and J. G. Williams, *Research Assistant*

This work was undertaken as a necessary preliminary to the evolution of a general iodimetric method for the estimation of carbonyl group content in organic compounds.

Iodine reacts with phenylhydrazine giving iodobenzene and hydriodic acid.[1] $C_6H_5NH.NH_2+2I_2=C_6H_5I+3HI+N_2$.

Consistent iodine values can readily be obtained for aqueous phenylhydrazine solutions, but only under certain conditions. The iodobenzene produced dissolves some iodine. The simplest method of titration is to add an excess of iodine, allow sufficient time for complete reaction, add an excess of thiosulfate, shake with a few cubic centimeters of ether, and finally titrate with iodine once more, using freshly prepared starch solution. Shaking with ether hastens the extraction of the iodine from the iodobenzene and hence expedites the determination. The ether does not affect the titration.

The presence of the sodium acetate[2] or other "buffer" salts usually recommended, such as sodium bicarbonate, borate or phosphate, slows down the reaction and gives low results. Addition of hydrochloric or sulfuric acid until the solution is just acid to methyl orange before beginning titration is all that is necessary to eliminate this source of error.

Aqueous solutions of phenylhydrazine or its salts change colour fairly rapidly and deposit a brownish substance. This change appears to take place more rapidly in daylight than in the dark. The hydrochloride does not change in iodine value at a rapid rate at room temperature, but at 60° the rate of decrease is far from negligible. The acetate, or hydrochloride with sodium acetate added, does decrease appreciably in iodine value at room temperature.

Two series of experiments were carried out in diffused daylight with approximately 0.1 *M* phenylhydrazine hydrochloride: (*a*) using boiled distilled water saturated with nitrogen and a nitrogen atmosphere; (*b*) distilled water saturated with oxygen and an oxygen atmosphere.

[1]von Meyer, *J. prakt. Chem.*, [2] **36**, 115 (1887).

[2]Fischer, *Ber.*, **17**, 572 (1884); **41**, 74 (1908).

Table I contains the results of these two series.

TABLE I

OXIDATION OF PHENYLHYDRAZINE HYDROCHLORIDE SOLUTION BY OXYGEN

Values in c.c. of 0.1 *N* iodine solution per 5 c.c.

	Room temperature, 21°		Water-bath, 60°	
Time	Series *a*	Series *b*	Series *a*	Series *b*
hours	Nitrogen	Oxygen	Nitrogen	Oxygen
0	18.35	18.35	18.35	18.35
0.25	.....	....	18.35	17.75
0.5	18.35	18.1	....	....
1.0	....	....	18.4	17.6
1.5	....	....	18.4	17.25
2.0	18.4	17.7	....	....
18	18.4	14.9	....	....

With oxygen the solutions became lemon yellow in 15 minutes, even at room temperature, and in 18 hours they had become very turbid. The samples under nitrogen remained colourless.

This factor does not appear to have been taken into account in any of the determinations of the carbonyl group given in the literature. As far as we can ascertain, attention has never before been directed to this phenomenon. In all our subsequent work oxygen-free water was used, and an atmosphere of nitrogen maintained.

For the investigation of hydrazone formation acetone was used. It has two advantages, namely, (*a*) its strength can be accurately determined by Messinger's method[3,4] and (*b*) it is readily soluble in water.

Hydrazones are rapidly attacked by iodine, due to the fact that hydrazone formation is a reversible reaction. We suspended a few drops of acetone-phenylhydrazone in water, added an excess of 0.1 *N* iodine solution and found the decomposition to be 80.6% in 15 minutes. With benzaldehyde-phenylhydrazone suspended in a mixture of 50% by volume of methyl alcohol and water the decomposition was 47.3% in the same time. The iodimetric determination of the unchanged phenylhydrazine, therefore, requires the removal of the hydrazone formed. Von Meyer's method disregards this fact. Since acetone-phenylhydrazone has, at room temperature, a solubility in water amounting to about 0.015 *M* concentration, centrifugal separation of the oil is not sufficient. The hydrazone can be removed by shaking with such solvents as ether, chloroform or benzene. These also extract some of the phenylhydrazine. Since in hydrazone extraction ether is the most efficient of the three solvents we tried, this was used. A correction, however, must be applied to the aqueous volume increase due to ether solution. A partition

[3]Ardagh, *Ind. Eng. Chem.*, **16**, 1133 (1924).

[4]Hermans, *Chem. Weekblad*, **18**, 348 (1921).

coefficient for phenylhydrazine in water-ether must be determined and a correction for the phenylhydrazine in the ether extract made. The fact that consistent results were obtained using various quantities of ether shows that the hydrazone partition between water and ether is such as to give virtually complete extraction.

Our method for determining the unchanged phenylhydrazine in the following series of determinations was the following:

Twenty-five c.c. of solution was pipetted into a nitrogen-filled separating funnel of about 75 c.c. capacity. To this was added enough ether to give a final ethereal layer of about 1 c.c. (usually 3-4 c.c. of ether was required) and the mixture was vigorously shaken for one minute. After two minutes had been allowed for separation, part of the aqueous layer was run out, 10 or 20 c.c. just acidified with hydrochloric acid (methyl orange) and the titration carried out as already described. The volumes of aqueous and ethereal layers were accurately determined by running the remainder of the liquid into a small calibrated measuring cylinder with wide readings. The partition coefficient for the phenylhydrazine in the ethereal layer must be determined on a blank carried out under the same conditions as in the experiment, and then the iodine value of the unchanged phenylhydrazine in the original 25 c.c. becomes a simple calculation. The partition coefficient for phenylhydrazine hydrochloride for ether-water is about 0.5, but the addition of sodium acetate increases this to 1.7 and under alkaline conditions it rises towards 3.0.

In the first series of experiments phenylhydrazine acetate was used because Michael[5] states that the hydrochloride reacts slowly or not at all with ketones. The phenylhydrazine acetate concentration in the reacting solution was approximately 0.04 *M* and the acetone 0.024 *M*. The rate of reaction is shown in Curve *a*, Fig. 1. To conserve space the calculations have been omitted.

It was qualitatively observed that the addition of sodium chloride increased the amount of hydrazone separated. The effects of various concentrations of sodium chloride were then tried quantitatively. The results are given in Curves *c*, *d*, *e* and *f*, Fig. 1.

The above results emphasize the fact that in the formation of hydrazone we are dealing with an equilibrium reaction. If it were possible to remove the hydrazone as formed, complete reaction could be secured. This cannot be done in the case of acetone with ether extraction because the ether also extracts unchanged acetone.

A greater concentration of sodium acetate than 20 g. per liter does not appreciably increase the yield of acetone-phenylhydrazone at equilibrium.

The favourable influence of sodium chloride in increasing the amount of hydrazone formed is no doubt due to a salting out of the hydrazone.

The effect of a 50 g. per liter concentration of sodium, potassium or ammonium chloride or sulfate on the equilibrium at the same concentration of 0.04 *M* for phenylhydrazine hydrochloride, and 0.024 *M* for acetone and 10 g. per liter for sodium acetate was found to be practically the same for each of these salts.

[5]Michael, *J. prakt. Chem.*, [2] **45**, 588 (1892).

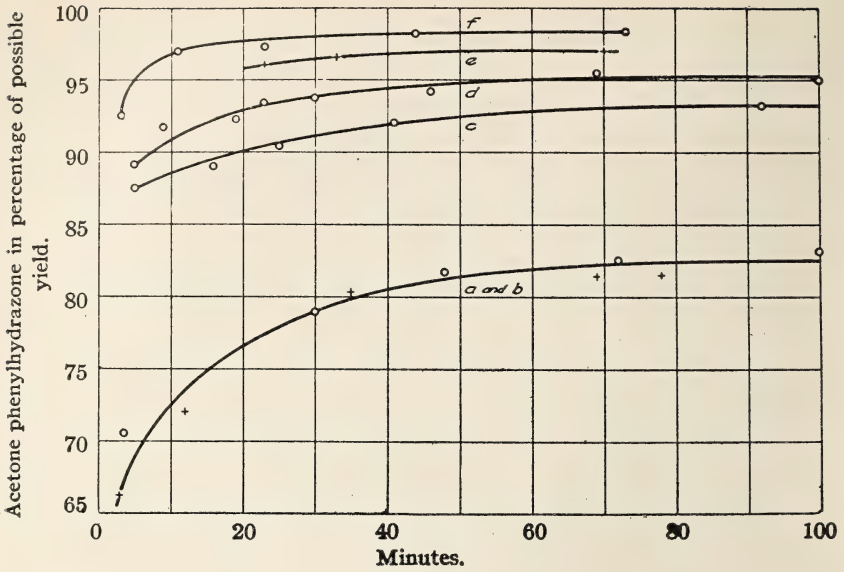


FIG. 1.

The addition of sodium acetate to phenylhydrazine hydrochloride greatly increases the amount of hydrazone formed. This appears to be due entirely, as will be shown later, to its "buffering" action.

In the straight reaction between the hydrochloride and acetone, hydrochloric acid is liberated as hydrazone formation proceeds, as shown by the following equation: $C_6H_5NH.NH_2.HCl + CH_3COCH_3 = (CH_3)_2C:N.NHC_6H_5 + H_2O + HCl$.

Hence the effect was tried of having acid and alkaline conditions initially present.

Twenty c.c. of 0.2 *M* phenylhydrazine hydrochloride, 20 c.c. of 0.12 *M* acetone and the recorded volume of 0.1 *N* hydrochloric acid or 0.1 *N* sodium hydroxide solution were added to a 100 c.c. flask and made up to the mark with air-free, distilled water. Between four and five hours was given for equilibrium to be reached.

The results are given in Table II and graphically in Fig. 2. The final concentration of acid and alkali has been calculated from the degree of reaction since, except where the reaction has gone almost to completion, it cannot be determined by direct titration owing to further reaction taking place. The Sörensen (P_H) values recorded were determined after equilibrium had been reached by comparison with standard buffer solutions, using for the purpose a suitable series of indicators. Titrations over the maximum part of the curve gave final results agreeing with calculated values.

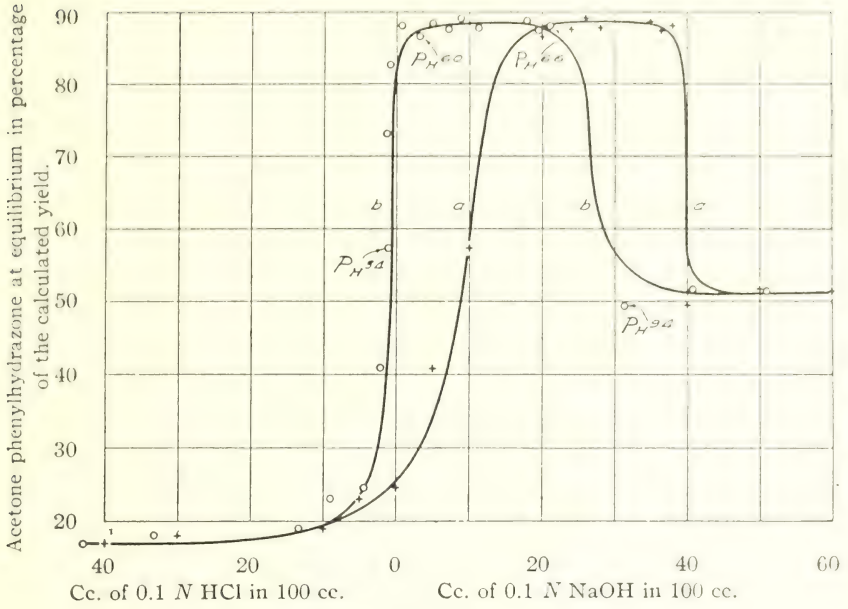


FIG. 2.

TABLE II

THE EFFECT OF ACIDITY AND ALKALINITY ON THE EQUILIBRIUM BETWEEN PHENYLHYDRAZINE HYDROCHLORIDE AND ACETONE AT 21°

1. Initial concn.,[a] c.c.					40.0[b]		30.0[b]	10.0[b]	5.0[b]	neutral
2. Amt. of hydrazone formed, %					17.1		18.1	18.95	23.0	24.55
3. Final concn.,[a] c.c.					43.0[b]		33.15[b]	13.3[b]	9.0[b]	4.3[b]
1.	5.0	10.0	20.0	22.0			24.0		26.0	28.0
2.	40.9	57.3	86.5	88.4			87.5		89.1	87.7
3.	2.15[b]	1.0[b] (PH 3.4)	3.4	5.0	(PH 6.0)		7.2		8.9	11.2
1.	30.0	35.0	36.5	38.0			40.0		50.0	60.0
2.	92.0	88.8	87.4	88.0			49.5		51.8	51.5
3.	12.3	18.0	19.7	21.1	(PH 6.6)		31.35	(PH 9.4)	40.95	51.0

[a] C.c. of 0.1 *N* acid or alkali per 100 c.c.

[b] These values are of c.c. of acid; the others are of c.c. of alkali.

In Table III, 0.05 *M* phenylhydrazine, 0.024 *M* acetone, some of the values enable us to locate additional points on the curve where they are most needed to determine its shape where the abrupt upward shoot occurs. These points have been indicated in Fig. 2 and show that at the instant the Sörensen value of the solution rises to 5, or thereabouts, the curve rises practically to a maximum and then continues horizontally until free caustic alkali is present at the final condition, when the curve falls again almost vertically.

From the table or graph it will be observed that there is an abrupt

change in equilibrium when between 38 and 40 c.c. of 0.1 *N* sodium hydroxide solution per 100 c.c. is present; that is, with a sodium hydroxide concentration of about 0.04 *M*. The concentration of the phenylhydrazine hydrochloride itself was 0.04 *M*. This indicates that the abrupt fall in equilibrium value is due to the presence of free sodium hydroxide.

TABLE III

THE EFFECT OF ALKALINITY ON THE RATE OF REACTION BETWEEN PHENYLHYDRAZINE HYDROCHLORIDE AND ACETONE AT 21°

Initial concn., c.c. per 100 c.c...	8.1[a]	10.5[a]	13.2[a]	15.8[a]	18.5[a]	26.0[a]	34.0[a]
Hydrazone formed, %, 10 min..	56.0	62.0	69.4	81.0	86.1	88.5	91.0
70 min..	58.5	68.2	73.0	82.5	88.0	91.0	93.0
Final concn., c.c. per 100 c.c....	3.6[b]	3.1[b]	1.2[b]	0.7	0.9[a]	7.8[a]	15.4[a]

[a]C.c. of 0.1 *N* NaOH. [b]C.c. of 0.1 *N* HCl.

It appears from these values that there is not any noticeable change in the rate of reaction, and the results accord with the rate curves in Fig. 1.

Shettle[6] states that the velocity of the reaction between acetone and phenylhydrazine decreases with the addition of small quantities of hydrochloric or acetic acid, and is reduced to zero on adding potassium hydroxide. This means that no hydrazone will be formed when free caustic alkali is present, which is certainly not the case under the conditions we used in carrying out our work. Our observations show that the presence of acid decreases the proportion of hydrazone formed, but not continuously with increase of acid. The presence of free sodium hydroxide also decreases the proportion of hydrazone formed, but to a less extent; it certainly does not reduce the velocity to zero.

A study of the reaction should be made to determine the shape of the "acetone phenylhydrazone-*P*H" curve. This, one of the authors hopes to do shortly. The shape of the curve may, of course, change to some extent for different ketones and aldehydes. This should also be investigated.

We had now gained the necessary insight into the chemistry of phenylhydrazine and the mechanism of hydrazone formation, as set forth in the opening paragraph of this paper.

Hydrazone formation is a reversible reaction peculiarly affected by hydrogen-ion concentration. The magnitude and range of this effect may differ with different carbonyl compounds, but it can be laid down definitely that the best condition for maximum formation of acetone phenylhydrazone is with a final Sörensen value between 5 and 7, in other words the solution should still be faintly alkaline to methyl orange

[6]Shettle, *J. Russ. Phys. Chem. Soc.*, **43**, 1190 (1911).

when the reaction has reached equilibrium. Further work and other experiments in the evolution of a general analytical method are given in the following paper.

The assumption that under certain conditions hydrazone formation is quantitative[7] is obviously not absolutely correct. If we look at the problem from the viewpoint of chemical dynamics, however, we perceive that the more insoluble the hydrazone the more probably the reaction will approach completion.

The Fehling's solution method of Benedikt and Strache,[8] which up to this date has been looked upon as a standard method for carbonyl group determination, assumes that the hydrazone reaction proceeds to completion under the conditions laid down for that method. The carbonyl compound, however, will not be completely converted into a hydrazone and, furthermore, the hydrazone formed will react with the Fehling's solution. These errors, it is true, will decrease in proportion as the insolubility of the hydrazone increases. Both errors tend to give low results. Atmospheric oxidation of the phenylhydrazine, on the other hand, tends to give high results and hence serves to counteract the other two errors.

Summary

1. The reaction between phenylhydrazine and iodine does not proceed normally in the presence of buffer solutions such as of sodium acetate, borate or phosphate. When a buffer is present, sufficient hydrochloric or sulfuric acid should be added to render the solution just acid to methyl orange.

2. Solutions of phenylhydrazine and its salts, especially the acetate, are fairly rapidly oxidized by exposure to air, even at room temperature.

3. Contrary to the general assumption, a very small change in the Sörensen value of the solution may very considerably affect the equilibrium in hydrazone formation.

4. Iodine solution rapidly attacks hydrazones, hence von Meyer's method,[1,9] is of little value. Petrenko-Kritschenko[10] does not appear to appreciate the speed of this reaction.

5. Defects in the standard Fehling's solution method for the determination of the carbonyl group are pointed out.

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[7]Meyer (Tingle), "Determination of Radicles in Carbon Compounds," John Wiley and Sons, **1908**, p. 79.

[8]Benedikt and Strache, *Monatsh.*, **14**, 270 (1893).

[9]Sudborough and James, "Practical Organic Chemistry," Blackie and Sons, Ltd. London, **1920**, p. 225.

[10]Petrenko-Kritschenko, *Ann.*, **341**, 150 (1905).

6. Acetone-phenylhydrazone formation can be forced almost to completion by adjusting the final Sörensen value of the solution to between 5 and 7, and at the same time salting out the hydrazone. If the hydrazone is now extracted by a selective solvent immiscible with water the reaction can be made practically quantitative.

AN ACCURATE GENERAL IODIMETRIC METHOD FOR THE QUANTITATIVE DETERMINATION OF THE CARBONYL GROUP IN ORGANIC COMPOUNDS

By E. G. R. Ardagh, *Associate Professor of Chemical Engineering*, and J. G. Williams, *Research Assistant*

There are to be found in the literature[1] a number of methods for the quantitative determination of individual aldehydes,[2,3,4,5] and ketones[2,4,6,7]. Owing to the greater reactivity of aldehydes as a class as compared with ketones more quantitative methods have naturally been proposed for the former. A few of these methods are applicable to the determination of a limited number of aldehydes and ketones. There are only two, however, that can in any sense be called general methods.

The one general method for the quantitative determination of the carbonyl group which has been considered by all chemists to be dependable is that of Benedikt and Strache.[8] This method, in which the excess of phenylhydrazine is oxidized by Fehling's solution and the liberated nitrogen measured, unfortunately gives only approximately correct results. The method, furthermore, is tedious and cumbersome. Its accuracy has been improved by Smith,[9] but even his results are merely close approximations. With *p*-nitrobenzaldehyde he obtained consistent results 4.3% low, and with hydroxybenzaldehyde his results were consistently 2.7% high. We subjected Smith's modification to a careful test with acetone and obtained results within only about 5% of the correct value.

E. von Meyer's method[10] has also been recommended as a reliable general method for the carbonyl group. Using acetone, we found that von Meyer's method gave much lower results even than Smith's modification of the Benedikt and Strache method.

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[1]Houben-Weyl, "Die Methoden der organischen Chemie," Georg Thieme, Leipsic, 2nd edition, **1921**, vol. 1, pp. 188 and 220.

[2]Lautenschläger, *Arch. Pharm.*, **256**, 84 (1918).

[3]Pauly, Schübel and Lockemann, *Ann.*, **383**, 288 (1911). Welmans, *Pharm. Ztg.*, **1898**, p. 634. Meyer, *Monatsh.*, **24**, 833 (1903). Burzeps, *Analyst*, **29**, 78 (1904).

[4]Ripper, *Monatsh.*, **21**, 1079 (1900).

[5]Lockemann and Croner, *Z. anal. Chem.*, **54**, 11, 22 (1915).

[6]Messinger, *Ber.*, **21**, 3366 (1888). Ardagh, *Ind. Eng. Chem.*, **16**, 1133 (1924).

[7]Sy, *J. Am. Chem. Soc.*, **29**, 786 (1907).

[8]Benedikt and Strache, *Monatsh.*, **14**, 270, 373 (1893).

[9]Smith, *Chem. News*, **93**, 83 (1906).

[10]von Meyer, *J. prakt. Chem.*, [2] **36**, 115 (1887).

These two are the only known methods for the determination of the carbonyl group that are looked upon as general methods. Our method resembles that of von Meyer in so far as the iodimetric determination of phenylhydrazine is concerned, but differs from von Meyer's in every other respect.

It is fairly obvious that the use of a hydrazine giving virtually insoluble hydrazones would largely solve the difficulties. We prepared a number of hydrazines in the hope of finding one that would give an insoluble acetone-hydrazone. We were not so fortunate as to discover such a one. We note, however, that Bülow[11] has recently succeeded in isolating a very insoluble acetone-hydrazone (acetone-2, 4-dinitrophenylhydrazone) and has applied it to the detection and estimation of small amounts of acetone in urine.

The study of the conditions for the maximum formation of acetonephenylhydrazone given in the preceding paper enabled us to develop a general method for the determination of the carbonyl group.

Attention is drawn in that paper to the necessity of preventing oxidation of phenylhydrazine through contact with air. Boiled distilled water must be used in the preparation of all solutions as well as for making up samples to a definite volume. An inert atmosphere must be kept in contct with the solutions at all stages. Furthermore, the hydrogen-ion concentration must be kept within certain limits. Finally the hydrazine $\rightleftarrows$ hydrazone reaction is reversible, so that theoretically complete reaction is impossible. However, by adjusting all the influencing conditions enumerated above to an optimum, and at the same time introducing the principle of salting out, together with extraction of the hydrazone by a selective solvent, the hydrazine $\rightarrow$ hydrazone reaction can be forced for all practical purposes to completion.

To maintain the Sörensen (P_H) value of the solutions between 5 and 7 any suitable buffer salt can be used. For our general method we selected disodium phosphate; the Sörensen value of the 0.1 N solution is 9.2 and that of the 0.1 N monosodium phosphate solution is 4. The hydrochloric acid liberated in the hydrazine $\rightarrow$ hydrazone reaction would result in a Sörensen value somewhere between these limits.

The partition coefficient of the phenylhydrazine hydrochloride between ether and water was determined by experiment to be 0.5. The addition of one equivalent of disodium phosphate increases this to 1.9, and six equivalents to 6.2.

Such high values necessitate so large a correction that, in order to work out a reliable analytical method, some more suitable solvent should be employed. This we found in petroleum ether.

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[11]Bülow, *Science*, **61**, 344 (1925).

Under certain circumstances it is obvious that the hydrazone reaction must of necessity be carried out in some organic solvent. Herein petroleum ether has the additional advantage of being practically immiscible with alcohol-water solutions of high alcoholic content. Forty per cent. by volume alcohol shows no change in volume on shaking with petroleum ether, and even with 70% by volume the change is very small.

The petroleum ether that we used was purchased from the J. T. Baker Chemical Company, who state that it is the fraction obtained between 40° and 60°. It had been distilled presumably from Pennsylvania crude oil. We shook it with bromine water until no more of this reagent was bleached by five minutes' shaking, then with water, then with 0.1 *N* sodium thiosulfate solution, and finally with water several times. A distillation test following the treatment with bromine water showed first drops over at 34° and the rest came over steadily with steadily rising temperature to 58°, except for a residue of less than 10%, of which half distilled very slowly with temperature rising to 67° and the remaining 5% did not distil even with the water boiling in the water-bath. This residue was miscible with petroleum ether but had a specific gravity slightly greater than water. It was probably brominated hydrocarbons.

As an extracting solvent petroleum ether is ideal in its low partition coefficient for phenylhydrazine. With a solution of 20 c.c. of 0.5 *M* phenylhydrazine hydrochloride, 20 c.c. of 0.5 *M* disodium phosphate solution, 40 c.c. of saturated sodium chloride solution, made up to 100 c.c., the partition coefficient was 0.055. This value changes very little with appreciable variation of conditions; using the same amount of phenylhydrazine hydrochloride and disodium phosphate, 30 c.c. of 95% by volume alcohol, 10 c.c. of saturated sodium chloride solution and then making up to 100 c.c., the value obtained was 0.052. In making a determination 25 c.c. was vigorously shaken with 4-5 c.c. of petroleum ether for two minutes. A period of two minutes was taken, because it was found that one minute of shaking does not suffice to extract the hydrazone from aqueous liquids.

The following is a detailed description of our general analytical process:

Distilled water boiled and cooled under a nitrogen atmosphere is used throughout. The carbonyl compound is weighed out; if liquid, by being sucked into a tared glass bulb which is then broken under water (or a mixture of alcohol and water) and the liquid made to a known volume. Approximately 0.5 *M* phenylhydrazine hydrochloride is made from recrystallized hydrochloride carefully dried and kept in the dark. Alternatively it can be made by carefully neutralizing a phenylhydrazine solution with hydrochloric acid. The 0.5 *M* sodium phosphate solution begins to crystallize at about 25°; hence a slightly weaker solution is advisable, somewhat more being taken.

For a determination 20 c.c. of phenylhydrazine solution, 20 c.c. of phosphate and sufficient carbonyl compound to react with about half the phenylhydrazine are mixed in

a 100 c.c. flask (flushed out with nitrogen) made up to the mark with saturated sodium chloride solution and allowed to stand, stoppered, at room temperature. Generally 30 minutes is sufficient for complete reaction. If a solid precipitate separates it should be filtered off as quickly as possible. Twenty-five c.c. of the aqueous solution is now placed in a cylindrical separatory funnel of about 75-100 c.c. capacity (flushed out with nitrogen) and 4-5 c.c. of petroleum ether is added. After two minutes of vigorous shaking, the petroleum ether is allowed two minutes to separate, and then some of the aqueous layer is run into a calibrated 25 c.c. cylinder. Ten c.c. of this is now pipetted into a 250 c.c. ground glass-stoppered Erlenmeyer flask (again in a nitrogen atmosphere), two drops of 0.1% methyl orange solution are added and then dilute acid—sulfuric or hydrochloric—drop by drop until the indicator just turns pink. Sufficient 0.1 *N* iodine solution is now added to give an excess of about 5 c.c. and the stoppered flask allowed to stand for five minutes to insure complete reaction between the phenylhydrazine and iodine. Freshly prepared starch solution is added and an excess (about 3-4 c.c.) of 0.1 *N* thiosulfate solution run in. About 5 c.c. of diethyl ether is now added and the whole shaken to dissolve iodine from the drops of iodobenzene. A final back-titration is now made with the 0.1 *N* iodine solution. The nitrogen atmosphere is especially necessary to prevent oxidation of hydriodic acid. The remainders of the aqueous and ethereal solutions are then run into the measuring cylinder and the volumes determined.

A blank under similar conditions is carried out on the phenylhydrazine alone. The partition coefficient can be determined by shaking for two minutes with petroleum ether and testing the aqueous layer. The rest is a simple calculation; 108 parts by weight of phenylhydrazine react with 28 parts by weight of the carbonyl group.

Details of Calculation for Acetaldehyde

The sample was taken from a bottle of Merck's absolute that had not been previously opened.

Wt. of bulb+acetaldehyde = 4.4516 g.
Wt. of bulb = 1.4773 g.

Acetaldehyde = 2.9743 g.
Volume of glass fragments = 0.5 c.c.
Therefore, concn. of acetaldehyde is 2.9743 g. in 99.5 c.c.
The iodine solution was 0.0995 *N*; the thiosulfate was exactly equivalent.
Amounts taken: 25 c.c. of 0.5 *M* phenylhydrazine hydrochloride soln.
20 c.c. of 0.5 *M* disodium phosphate soln.
10 c.c. of acetaldehyde soln.
45 c.c. of saturated sodium chloride soln.

100 c.c.

A dense, white emulsion immediately separated, later forming a solid. After 30 minutes at room temperature the solution was filtered and 25 c.c. of the filtrate extracted with petroleum ether. This gave an aqueous layer of 24.9 c.c. and a petroleum-ether layer of 3.2 c.c. Ten c.c. of the aqueous layer was taken, 30 c.c. of iodine added, the mixture allowed to stand as described and then 12 c.c. of thiosulfate solution was run in; 2.65 c.c. of iodine solution was now required to produce a blue colour with starch. The net amount of iodine required was, therefore, 20.65 c.c. The blank on the phenylhydrazine alone was 47.55 c.c. of iodine. The partition coefficient for the phenylhydrazine in water-petroleum ether was 0.055.

The corrected value for iodine required by the 10 c.c. aliquot portion extracted = ([24.9+(3.2×0.055)]/25.0)× 20.65=20.70 c.c.

The weight of hydrazone formed and removed by filtration (calculated) = 1.040 g. (say, 1.0 c.c.). Correcting the iodine value for this gives 99/100×20.70=20.45 c.c.

The iodine value for 1 c.c. of acetaldehyde is, therefore, 47.55−20.45=27.10 c.c. of 0.0995 *N* iodine solution.

$CH_3CHO \equiv C_6H_5NHNH_2 \equiv 2I_2$. Therefore, 44.04 g. of acetaldehyde≡40 liters of 0.1 *N* iodine solution, or 1 c.c. of 0.1 *N* iodine solution indicates 0.001101 g. of acetaldehyde.

Acetaldehyde found per c.c. =27.1×0.995×0.001101 g. =0.02969 g.

Acetaldehyde taken per c.c. =2.9743/99.5=0.02989 g.

The corrections for partition coefficient and change in aqueous volume when pretoleum ether is employed are so small that for many purposes they can be safely ignored.

This simplification eliminates both the determination of the partition coefficient and of the change in volume of the aqueous layer. In consequence it greatly shortens the necessary figuring, especially when we also leave out of our calculations the correction for volume of glass fragments and volume of hydrazone filtered off. In this way the time required to carry out the determination and to make the calculation is greatly cut down.

The determination of acetaldehyde described above is shortened under this simplified procedure to the following:

Blank on phenylhydrazine	47.5 c.c. of 0.995 *N* iodine soln.
Aqueous extract	20.6 c.c.
Iodine equivalent of acetaldehyde in 10 c.c.	26.9 c.c.

26.9×0.995×0.001101=0.02947 g. of acetaldehyde per c.c. Error due to simplified procedure: 0.2969-0.2947=0.0022 g. or 0.74% of the amount of acetaldehyde found by the long method.

For the sake of space further calculations have been omitted. The solvent for the benzaldehyde was 60% by volume alcohol, while for the acetophenone 40% by volume alcohol was employed.

The examples given serve to show in what manner the authors' general method can be modified. It will be seen that when the substance to be analyzed is not soluble in water, alcohol of suitable strength can be substituted for the water. In the compounds determined petroleum ether and water, or alcohol-water, sufficed. But the principles of the method are quite general and hence one is not restricted to petroleum ether as the hydrazone solvent or to alcohol-water as the solvent for the carbonyl compound. Any solvent that will extract hydrazones from other solvents can be used.

Following the general practice the authors have employed phenylhydrazine hydrochloride which necessitates the use of a buffer salt to control the Sörensen value. It will be realized from the first paper that

in normal cases solutions of the phenylhydrazine base itself can be used. This may in certain cases offer decided advantages; for example, when a high percentage of organic solvent is necessary to keep the ketone or aldehyde in solution.

Table I gives the results obtained with a few additional compounds. The last three substances in the table were not specially purified samples.

TABLE I

TYPICAL RESULTS

Compound	Acetone	Benzaldehyde	Acetophenone	Diethyl ketone	Ethyl aceto-acetate	Citral
Wt. taken, g.	0.02980	0.05227	0.0675	0.0291	0.0545	0.0603
Wt. found, g.	.02991	.05222	.0672	.0287	.0560	.0600

In the case of benzophenone the reaction proceeds at an exceptionally slow rate. Trials were made using alcohol-water and allowing the mixture to stand for periods of time up to 24 hours and also heating on the water-bath for one hour. The characteristic needle-like crystals of benzophenone-phenylhydrazone were obtained, but the extent of formation was only 10-15%. Butyl alcohol was also tried without success. Further work will be done on this compound. The presence of one phenyl group in a ketone (acetophenone) slowed down the rate of reaction considerably (two hours at room temperature was required). It appears that ketones with two aromatic radicals react very slowly indeed, and it may require particular conditions of high concentration and temperature and possibly also control of the Sörensen value within narrower limits to secure a high degree of reaction in a reasonable time.

The slow rate of reaction in the case of such compounds as acetophenone and benzophenone may reasonably be attributed at least in part to steric hindrance. The senior author proposes in the near future to carry out a series of investigations upon the rate of hydrazone formation under various conditions, and also upon the application of the general method to the determination of aldehydes and ketones in the presence of one another and its application to the analysis and valuation of many substances of commercial importance.

SUMMARY

1. A general method of a high degree of accuracy for the determination of the carbonyl group in organic compounds has been worked out.

2. Further interesting fields to which this general method can be applied have been pointed out.

DISTILLATION OF ACETATE OF LIME

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A. D. Barbour, G. E. McClellan, and E. W. McBride,
Research Assistants

Anyone who has had occasion to consult the literature dealing with the manufacture of acetone by the dry distillation of acetate of lime must have been struck, not only by the vagueness of the descriptions and the paucity of the figures, but also by statements that are actually incorrect. A few of such statements which the writers have come across in articles written by some of the best known authorities are given here:

Acetone is made by the dry distillation of gray acetate of lime at 290° to 400° C.[1]

Large quantities (of acetone) are made from gray acetate of lime by dry distillation at high temperature. **The distillation takes place in three stages. At first water containing a small percentage of acetone comes over, in the second stage when the temperature of the mass has risen to 400° C. acetone oils are obtained.[2]

To secure a maximum yield of acetone, the points to be attained are uniformity of temperature throughout the whole mass and slow heating to not over 300° C.[3]

The conversion into acetone is effected by simply heating the acetate at about 300° C. **The decomposition of the acetate does not become active until the temperature reaches about 380° C., the bulk of the distillate comes over between 380° and 400° C.[4]

Barium acetate decomposes at 400° to 405° C., calcium acetate at a higher temperature, while the most suitable temperature for decomposition of acetic acid to yield acetone is 500° C.[5]

Acetone is usually prepared by the dry distillation of barium acetate at a moderate heat. Calcium acetate can also be employed, but the temperature required is greater, and the product is contaminated with impurities, such as dumasin, an isomeride of mesityl oxide.[6]

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[1]Rogers, "Manual of Industrial Chemistry," 1915, p. 543.

[2]Veitch, "Chemical Methods for the Utilization of Wood," *U.S. Dept. Agr., Circ* 36 38 (1907).

[3]Sadtler, *J. Soc Chem. Ind.*, **8**, 1008 (1889).

[4]Marshall, "Explosives," Vol. I, p. 341.

[5]Squibb, *J. Soc. Chem Ind.*, **15**, 612 (1896).

[6]Thorpe, "Dictionary Applied Chemistry," Vol. I, **1912**, p. 21.

In view of the indefiniteness of certain of these statements and the conflict of several others, it seemed that an investigation of this important industrial process would be well worth while.

Owing to the complex character of commercial gray acetate of lime, it was thought advisable to begin the investigation using pure calcium acetate. The gray acetate of lime of commerce "generally contains 80 to 82 per cent. of calcium acetate as determined by analysis, and 4 to 7 per cent. of water, the remainder being made up of various impurities. Of the 80 to 82 per cent., however, several per cent. consist of formate, propionate, and salts of other organic acids."[7] When formates are present dry distillation gives aldehydes. If propionates are present we get methylethyl ketone and diethyl ketone. Higher homologs yield the corresponding higher ketones. This, however, is not the whole story. Ketones and aldehydes polymerize at high temperatures to give oily substances of high boiling point. Furthermore, any free lime in the gray acetate, resulting from slightly over-liming before distilling the methanol and acetone, reacts with calcium acetate in the retort to give methane.

APPARATUS

The apparatus was set up as shown in the accompanying diagram. The alundum muffle, $3\frac{3}{4} \times 5\frac{1}{2} \times 12$ inches, was wound with 20 feet of nichrome No. 2 wire, 17 B. & S. gauge, held in place with alundum cement. The windings were spaced somewhat wider at the centre to give a uniform temperature in the muffle. The resistance of the muffle when cold was 7.5 ohms; when heated to 450° C., 7.8 ohms. The muffle was housed in a 12-inch length of 12-inch diameter steel pipe closed at the ends with discs cut from asbestos-cement board in which rectangular openings were cut to hold the muffle in the centre of the housing. Kieselguhr was used as packing around the muffle. In starting a heat the current was adjusted to 10 amperes, which raised the temperature of the muffle to 450° C. in about 45 minutes. From this stage 6.7 amperes would maintain the temperature at 430° C., 7.0 at 450° C., and 7.6 at 490° C. The first hour recorded in the tables was timed from the moment the temperature reached that given for the particular run. Since about 5 minutes were required for the temperature to rise from 400° C., the temperature at which acetone begins to form at an appreciable rate, to 430° C., the first hour in the record refers to a period in reality somewhat longer than an hour.

The tube in which the calcium acetate was heated was made of ordinary soda glass with an outside diameter of $1\frac{3}{8}$ inches. Its length

[7] *J. Soc. Chem. Ind.*, **10**, 166 (1891).

over all was 22 inches, and it was drawn down at the end next the receivers to a long, narrow tube, which was inserted for about 1 inch into the inlet tube of the first receiver in order to prevent any contact between the acetone vapour and the rubber connection. Pieces of asbestos board with circular holes cut to fit the glass tube were fastened to the ends of the furnace in such a way as to hold the tube as nearly as possible in the axis of the muffle. The boat carrying the 2-gram charge of calcium acetate was a 6-inch length of soda glass tubing of such diameter as to fit the tube snugly. The charge was spread out as evenly as possible over the bottom of the boat.

A stream of nitrogen was employed to flush out the acetone vapours from the heated zone and to carry them to the receivers.

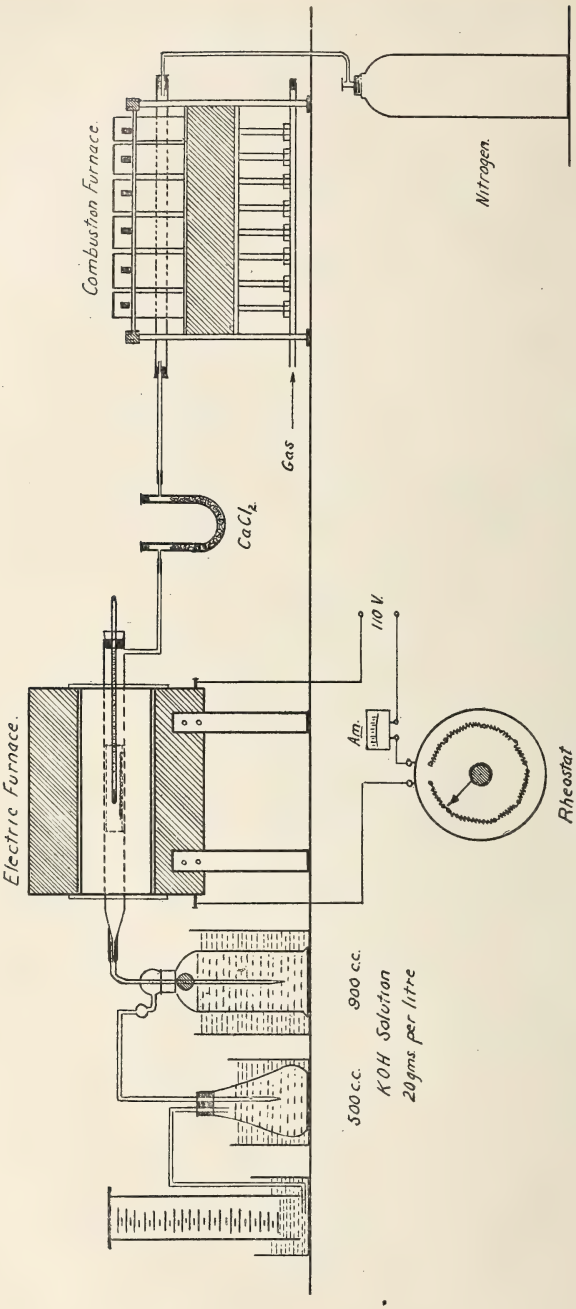
The first receiver was a ground-glass stoppered wash bottle of 1000-cc. capacity. It carried a stoppered side tube on the shoulder, from which samples could be taken at any time. The tube leading to the bottom of the wash bottle was drawn down to a rather fine jet so that the gases would issue in a stream of fine bubbles. To absorb the acetone from a run, 900 cc. of dilute potassium hydroxide (20 grams KOH made up to 1,000 cc.) were used, and the wash bottle was kept cold by surrounding it with ice and water. The acetone was usually almost completely absorbed in the first receiver.

The graduated cylinder shown in the diagram beyond the second receiver was used from time to time to determine, within about 50 cc., the rate of the gas stream in litres per hour.

At the outset a nitrogen-filled glass thermometer scaled to 500° C. was used to register the temperature. Owing to the difficulty of determining with sufficient accuracy the correction to be made for the long column of mercury extending beyond the muffle, a base metal thermocouple was soon substituted. To keep the cold junction from warming up a water jacket was placed around the metal housing protruding from the muffle and a flow of tap water was kept circulating through this cooling jacket. The thermocouple with its instrument was checked against a platinum-platinum-rhodium thermocouple and galvanometer, calibrated by the Bureau of Standards. The two checked within 1° C. for all readings up to 450° C.

METHOD OF DETERMINING ACETONE

It is obvious that if the results are to be of any value whatever the method of determining the acetone produced must be thoroughly dependable. Of the methods that have been worked out for the determination of acetone, Messinger's volumetric method is the one most usually



APPARATUS FOR DISTILLATION OF CALCIUM ACETATE

employed. Many modifications of this method are to be found in the literature. Two of the best descriptions are those by Collischonn[8] and by Griffin.[9] After trying out some of the methods recommended, Griffin's method was selected as the most satisfactory for the present purpose. This was carried out as follows:

By means of a standardized pipette 50 cc. from the ice-cold solution in the receiver were transferred to a 250-cc., ground-glass stoppered flask, and a measured amount of standard iodine solution (approximately 0.1 *N*) known to be an excess was added slowly (not faster than 50 cc. in 3 minutes) and with constant shaking. The mixture was then allowed to stand for 5 minutes, acidified with 1 *N* hydrochloric acid to liberate the excess of iodine, and titrated immediately with standard thiosulfate (approximately 0.1 *N*). About 2 cc. of freshly prepared and filtered starch solution were added just before the yellow colour of the iodine disappeared. The thiosulfate was standardized against resublimed iodine that had been dried over calcium chloride and once more carefully sublimed. The iodine solution was then checked against this standard thiosulfate solution. Standardized burettes were used. Duplicate determinations always gave checks within 0.05 cc.

In making up the acetone solution of known concentration to be used as a standard for the purpose of ascertaining if that calculated from the amount of iodine taken up, as indicated in Equation 1, coincided with the actual quantity of acetone

$$(CH_3)_2CO+6I+4KOH=CHI_3+3KI+KC_2H_3O_2+3H_2O \qquad (1)$$

known to be present, the following procedure was adopted:

A very thin glass bulb, about 5-cc. capacity, was blown, a thin tube about 2 inches in length being left on each end. The bulb was then carefully weighed. Some of Kahlbaum's acetone was dried over calcium chloride and redistilled carefully. The small bulb was nearly filled with this acetone by suction, the ends were sealed off and when cool weighed again. The bulb was transferred to a 500-cc. glass-stoppered flask which had been standardized, about 200 cc. of water added, the bulb crushed with a long glass rod, the flask made up to the mark with water, the contents mixed thoroughly, and by means of standard pipettes several different quantities were taken for titration. After as many titrations as were required had been made, the volume of the glass fragments was determined and a correction made therefor. In every case the results agreed perfectly with the acetone calculated from the amount of iodine taken up.

[8] "Technical Methods of Analysis," **1921**, p. 72.

[9] *J. Chem. Soc.* (*London*), **81**, 350T (1902).

After carrying out a number of titrations, it was concluded that the points to be especially kept in mind if dependable results are to be secured by Messinger's method are the following:

(1) The iodine must not be added more rapidly than 50 cc. in 3 minutes.

(2) The flask must be shaken vigorously and continuously during the addition of the iodine.

(3) After running in the iodine, the solution must be allowed to stand at least 5 minutes before the hydrochloric acid is added.

(4) Sufficient hydrochloric acid must be added to liberate all the iodine that has not reacted with the acetone to form iodoform.

(5) The solution must be kept cold.

(6) The starch solution must be fresh and free from turbidity.

The reactions that take place in Messinger's method are expressed by the following equations:

$$2KOH + I_2 = KIO + KI + H_2O \qquad (2)$$

$$(CH_3)_2CO + 3KIO = CHI_3 + KC_2H_3O_2 + 2KOH \qquad (3)$$

Equations 2 and 3 will be found combined in Equation 1, from which it is seen that 761.52 grams of iodine react with 58.05 grams of acetone.

$$KIO + KI + 2HCl = 2KCl + I_2 + H_2O \qquad (4)$$

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI \qquad (5)$$

Interfering Reactions to be Considered

Unfortunately, acetone is not the only substance to be considered that might be present and that will, if present, absorb free iodine. Other ketones and, furthermore, aldehydes may be present, and all these substances will react with free iodine.

It is well known that acetone polymerizes under certain conditions, and that aldehydes are formed by heating together calcium formate and the calcium salts of acetic acid and other acids of this series. For example, a mixture of calcium formate and calcium acetate gives acetaldehyde on heating.

An attempt was made to minimize polymerization by using a glass tube, boat, and absorption vessel. At the outset an iron tube and boats made from sheet copper or from sheet aluminium were used. The boats were quite strongly corroded. This may have resulted from the free acetic acid present in the calcium acetate.

Preparation of Pure Calcium Acetate

To eliminate the formation of aldehydes and ketones other than acetone, some C. P. acetic acid (from which the calcium acetate was made) was further purified by freezing till about two-thirds had solidified,

and then pouring off and discarding the liquid portion. This was done three times. In this way any formic acid that might have been present was removed. It is a question, however, if this precaution was really necessary, since on testing the stock acetic acid in the usual way with mercuric chloride for formic acid the result was negative. Pure calcium carbonate was then added until a small quantity remained undissolved, the still slightly acid liquid filtered, and evaporated on a sand bath till a surface crust formed. The evaporation was finished on a water bath. The mass was then dissolved in hot water and evaporated until a thick, crystalline crust formed. This crystalline mass was removed and dried, first on a water bath and then overnight in a de Khotinsky double-walled electric oven at 120° C. In this way a calcium acetate was prepared that was free from other organic calcium salts and basic salts.

The preparation of anhydrous calcium acetate even from pure acetic acid and pure calcium carbonate is not a simple task, notwithstanding Lumsden's contentions.[10] The writers dried their pure acetate as already described at 120° C., overnight. Since pure acetic acid boils at 118° C., they thought the excess of acetic acid could be driven off completely at this temperature. The product obtained did not lose weight when kept at room temperature for 2 weeks over concentrated sulfuric acid, but when heated to 150° C. for 24 hours in a current of dry nitrogen it lost several per cent. of its weight. On condensing the vapours evolved a colourless liquid was obtained which appeared to be water and acetic acid. It did not contain any acetone or other substances that react with iodine. The acetate heated to 150° C. retained its whiteness and was completely soluble in water, giving a solution neutral to phenolphthalein. The loss in weight was 3.5 per cent. of the weight at 120° C. When heated to 200° C. the material became gray, much of it was insoluble in water, and the watery extract was alkaline to phenolphthalein. The loss in weight was 7.5 per cent. of the weight at 120° C.

To determine at what temperature acetone begins to come off, 2 grams of the material were heated in the muffle in a current of dry nitrogen, the gas being passed through the wash bottle at the rate of 2 litres per hour as in the quantitative work. Traces of acetone first made their appearance just about 160° C.

To check the figures obtained, the 120° C. and 150° C. products were analyzed, calcium being determined by titrating the oxalate with permanganate standardized against Kahlbaum's *pro analysi* sodium oxalate, acetic acid by distillation with phosphoric acid and titration

[10] "Technical Methods of Chemical Analysis," Vol. III, p. 306.

with 0.5 *N* potassium hydroxide, and water by difference. In making the acetic distillation with phosphoric acid, the distillation must be carried out very slowly, preferably on a sand bath, and the mass should not be heated to too high a temperature; otherwise there is danger of carrying over traces of phosphoric acid. Neither Lunge[10] nor Scott[11] sounds a warning note here.

Carrying out this method of analysis using a 1-gram sample for acetic acid and a 0.3-gram sample for calcium, the following figures were obtained:

	I	II
	Grams	Grams
Ca	0.0699	0.0699
$HC_2H_3O_2$	0.720	0.724

Calculating the calcium as $Ca(C_2H_3O_2)_2$ and the remaining $HC_2H_3O_2$ as free acid:

Calcium acetate dried at 120° C.

	I	II
	Per cent.	Per cent.
$Ca(C_2H_3O_2)_2$	92.0	92.0
$HC_2H_3O_2$	2.0	2.4
H_2O	6.0	5.6
	100.0	100.0

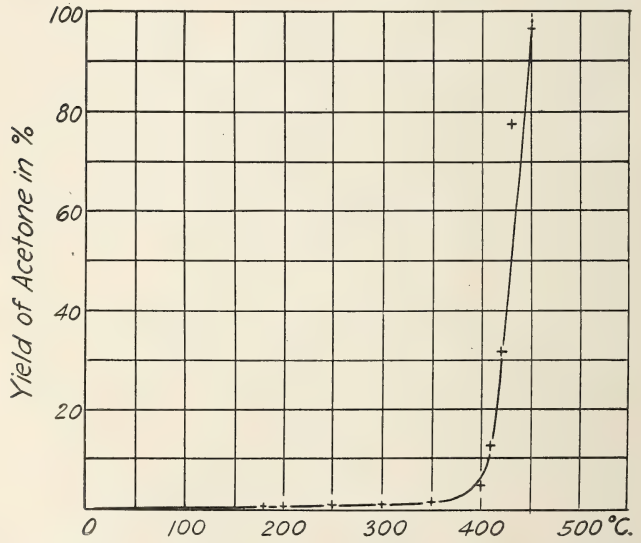


Fig. 1.—Yield of Acetone in 1 Hour at Different Temperatures. Gas Flow 2 Litres per Hour.

[11] "Standard Methods of Chemical Analysis," Vol. II, 3rd ed., p. 1057

If the water is present in the compound calcium acetate monohydrate, the foregoing figures may be expressed as follows:

	I	II
	Per cent.	Per cent.
$Ca(C_2H_3O_2)_2.H_2O$	58.6	54.8
$Ca(C_2H_3O_2)_2$, anhydrous	39.4	42.8
$HC_2H_3O_2$	2.0	2.4
	100.0	100.0

On analyzing in exactly the same way the material dried for 24 hours at 150° C., by which it had lost 3.5 per cent. of its weight at 120° C., its composition was found to be:

Calcium acetate dried at 150° C.

	I	II
	Per cent.	Per cent.
$Ca(C_2H_3O_2)_2$	95.2	95.2
$HC_2H_3O_2$	2.45	2.55
H_2O	2.35	2.25
	100.0	100.0

Assuming the water to be present as monohydrate:

	I	II
	Per cent.	Per cent.
$Ca(C_2H_3O_2)_2.H_2O$	20.65	19.75
$Ca(C_2H_3O_2)_2$, anhydrous	76.9	77.70
$HC_2H_3O_2$	2.45	2.55
	100.0	100.0

The water content has fallen, but not the free acetic acid.

On drying at 160° C. for 12 hours longer and analyzing the product, the following results were obtained:

	I	II
	Per cent.	Per cent.
$Ca(C_2H_3O_2)_2$	97.9	97.9
$HC_2H_3O_2$	1.95	2.0
H_2O	.15	0.1
	100.0	100.0

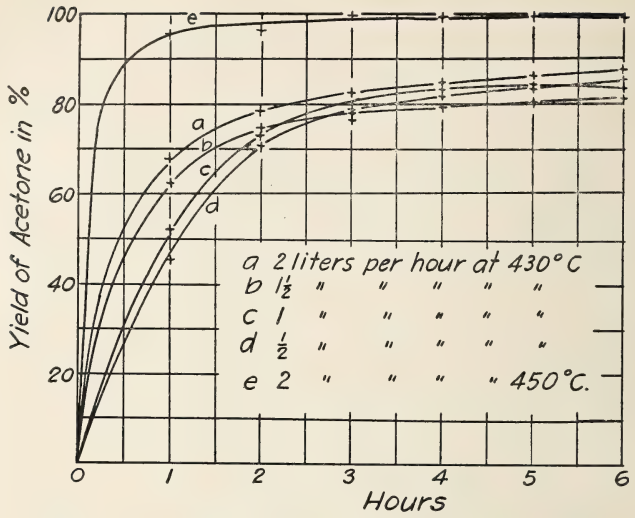


Fig. 2 —Acetone Yields at Varying Rates of Gas Flow.

Assuming the water to be present as monohydrate:

	I	II
	Per cent.	Per cent.
$Ca(C_2H_3O_2)_2.H_2O$	1.5	0.9
$Ca(C_2H_3O_2)_2$, anhydrous	96.55	97.1
$HC_2H_3O_2$	1.95	2.0
	100.0	100.0

The water was obtained by difference as before. Since the figure is so very small, it is quite possible that there is no water present at all, and that the material contains only anhydrous calcium acetate and free acetic acid. The remaining free acetic acid cannot be driven off by heating without the liberation of some acetone. Furthermore, the material dried at 160° C. is very hygroscopic.

Taking these points into consideration, it was decided to carry on an investigation with the material dried at 120° C., which is 92.0 per cent. $Ca(C_2H_3O_2)_2$. The material dried at 160° C. to 98.0 per cent. $Ca(C_2H_3O_2)_2$ still contains about 2 per cent free acetic acid. It is quite improbable that this free acetic acid yields acetone. In all probability it is driven off as acetic acid well below the temperature at which acetone would be formed by its decomposition.

Since 100 grams of the 120° C. product contain 92 grams of $Ca(C_2H_3O_2)_2$, the 2-gram sample contains 1.84 grams of $Ca(C_2H_3O_2)_2$.

Hence the yield must be multiplied by 2/1.84, or 1.087, to give the theoretical yield. This yield in per cent. appears in the final column of the tables. The figure in this column also contains a proportional amount of the acetone found (if any) in the second receiver at the end of the run. For example, when the second receiver was found to contain at the end of the run 0.7 per cent. of the theoretical yield, and the first receiver about 90 per cent. throughout, the 0.7 per cent. was distributed over the 7 hours in the proportion of 0.1 per cent. per hour. With Run 20 at 450° C. as an illustration, it is noted that at the end of

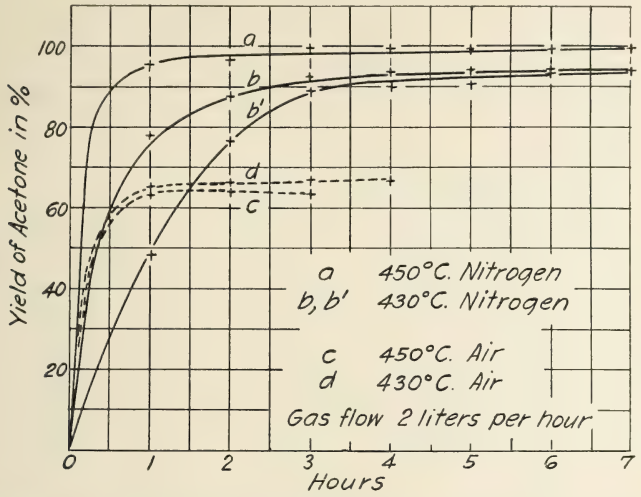


Fig. 3 —Comparison of Yields Using Nitrogen and Air. Curve b' Illustrates Variations Frequently Obtained in First Two Hours of Duplicate Runs.

7 hours the second receiver contained 0.74 per cent. of the theoretical yield of acetone. $0.74 \div 7 = 0.11$ per cent. Consequently, 0.11 per cent. is the proportion of acetone carried over each hour into the second receiver. The theoretical yield of acetone at the end of the sixth hour is therefore $[90.4 + (6 \times 0.11)]$ 1.087 or 98.8 per cent., and at the end of the seventh hour $[90.8 + (7 \times 0.11)]$ 1.087 or 99.5 per cent.

In answer to the inquiry, "How do you know that there is nothing in your receiver that reacts with iodine except acetone?" a distillation was run at 450° C. for 1 hour with a gas flow of 2 litres per hour, using distilled water only in the receivers. At the end of the run 500 cc. were transferred from the first receiver to a distillation flask, about one-half was distilled off and the distillate tested for aldehydes with ammoniacal silver oxide in the usual way and with 0.1 N potassium

permanganate. The same tests were carried out on the residual liquid. The test for aldehydes was negative in both cases. The residual liquid required about 25 minutes to decolorize one drop of 0.1 *N* potassium permanganate, the distillate decolorized only three or four drops of the potassium permanganate within about 0.5 minute. This is fairly good evidence of the absence of more than a trace of any substance that will register as acetone. In addition, an iodine absorption test was run on the residual liquid. A very small amount of iodine was taken up—by 100 cc. of the residual liquid a quantity of iodine indicating 0.00077 gram of acetone. Even if the substance (or substances) reacting with the iodine is not a trace of acetone remaining in the distillation flask, but some substance with a higher boiling point—for example, a polymerized product, the result of heating acetone to such a high temperature—the quantity present is too small to affect the results.

EXPERIMENTAL

In the experimental work there was at first great difficulty in securing concordant results. Usually, the yields of acetone obtained during the first hour of two duplicate runs would differ, often quite widely. This was not surprising, because concordance at this stage requires identical conditions of temperature, rate of gas flow, and time. Frequently, however, the total yield of acetone obtained in one run would be 10 or 15 per cent. higher or lower than the yield given by the duplicate run. A study of the influence of conditions upon the total yield of acetone brought out the facts that low yields resulted from starting the gas flow only after the charge had been heated to 400° C. or over, or by using a slow rate of gas flow. At high temperatures, such as 450° or 490° C. (the highest temperature used in this work), the influence of these two factors became still more pronounced. Still lower yields are obtained if the charge is allowed to remain some time, say 30 minutes, at a high temperature, say 450° C., before the gas flow is started. No doubt, at this temperature polymerization of the acetone in the vapour state proceeds quite rapidly.

By blowing out the acetone with dry nitrogen, as fast as it formed, it was possible to secure total yields that agreed very closely. With the apparatus used this necessitated a rate of 2 litres per hour. Lower rates gave lower total yields.

To get yield-time curves that present close agreement throughout, it is necessary to adjust the gas flow to the same rate in each run.

In order to bring out the influence of the factors mentioned above, as well as the influence on the yield of the presence of copper or iron,

and the yields obtained when air or carbon dioxide was substituted for nitrogen, the accompanying tabulated results have been prepared. These have been classified into different series, each of which illustrates the effect of varying one condition. In order to present the results in graphic form as well as to compare or to contrast on one sheet of paper the results obtained by changing one condition, four graphs have been prepared.

In most of the runs a very decided blackening of the charge occurred. This blackening was greatest at the end nearest the nitrogen inlet, and shaded off uniformly to a cream colour at the end nearest the receivers. The blackening was not confined to runs in which a low yield had been obtained.

If the black consists of a deposit of carbon or dark-coloured polymerized product surrounding the particles of calcium carbonate, evidently

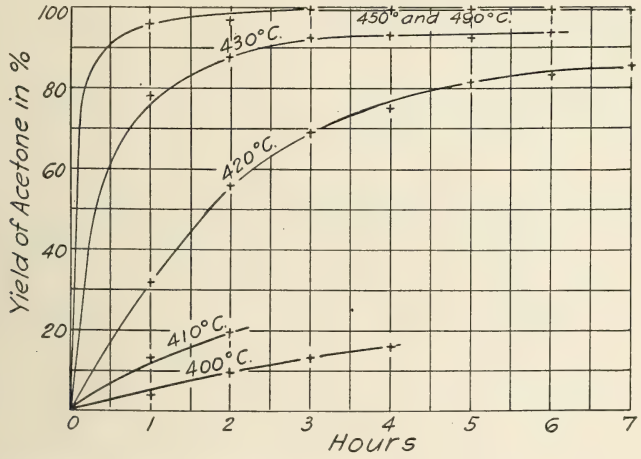


Fig 4 —Acetone Yields at Varying Temperatures. Gas Flow 2 Litres per Hour.

very little of it is necessary to render the charge dark in colour. The writers have not been able to account satisfactorily for the fact that this blackening is greatest at the end farthest removed from the receivers.

When a high yield during the first hour and a high total yield were obtained, the residue was uniformly cream coloured, with a slightly darker shade at the inlet end. Occasionally, for some reason not yet explained, very low yields were obtained and at the same time a blackening of the residue throughout its whole length.

The theoretical loss in weight for a 2-gram sample of the acetate should be 0.835 gram. The 2-gram sample contains only 1.84 grams

of $Ca(C_2H_3O_2)_2$. In other words, there will be a loss in weight of 0.16 gram due to the moisture and free acetic acid present. This will be a constant for every sample. The theoretical loss in weight when 1.84 grams of $Ca(C_2H_3O_2)_2$ are transformed to calcium carbonate is 0.675 gram. These together make 0.835 gram. The loss of carbon dioxide due to the production of calcium oxide is very small. In two cases it was found to be in the neighbourhood of 4 mg. The loss in weight in these experiments never amounted to 0.835 gram, the greatest being 0.810 gram. Usually this loss was in the neighbourhood of 0.800 with a variation of a few milligrams in both directions.

SERIES I—This series shows very conclusively that a temperature well above 400° C. is necessary before acetone begins to form rapidly from calcium acetate.

SERIES II—This series brings out the influence of rate of gas flow, especially on the first hour's yield.

SERIES III—Here we see how the total yield falls off (as compared with the yields obtained in Series V) when the acetone vapours are allowed to remain in the retort instead of being removed as fast as formed. At 450° and 490° C. the destruction of the acetone is more rapid than at 430° C.

In Run 9 a small quantity of oily liquid condensed just outside the furnace at the end next the receivers. This suggests polymerization.

Run 11 shows that when carbon dioxide is used in place of nitrogen to flush out the acetone vapours an equally good yield is obtained.

SERIES IV—It is evident from these runs that when air is used to flush out the acetone vapour low yields result.

SERIES V—Metallic iron and copper appear to have very little influence on the yield of acetone, even when a large surface of the metal is in direct contact with the acetate. The corrosion of the copper and aluminium boats previously mentioned may have resulted from the free acetic acid present in the calcium acetate.

SERIES VI—This series brings out the fact that between 450° and 490° C. practically a theoretical yield of acetone can be obtained from calcium acetate, provided the acetone vapours are flushed out by an inert gas, such as nitrogen, as quickly as they are formed.

SERIES I

Total hours	Temp. ° C.	Iodine added Cc.	Equivalent 0.1 *N* iodine Cc.	Thio required Cc.	0.1 *N* thio required CC.	0.1 *N* iodine taken up Cc.	Acetone in sample Grams	Acetone in first receiver Grams	Total yield acetone Grams	Apparent yield Per cent.	True yield from actual acetate in charge Per cent.
				Run 1.	*Temperature, 400° C.*		*Flow of nitrogen, 2 litres per hour*				
1	..	15	16.55	15.50	15.02	1.53	0.00149	0.0268	.. + .. = 0.0268	3.64	3.95
2	..	15	16.55	13.30	12.88	3.67	0.00356	0.0641	0.0641 + 0.0015 = 0.0656	8.94	9.72
3	..	25	27.58	23.65	22.92	4.66	0.00452	0.0814	0.0814 + 0.0051 = 0.0865	11.8	12.9
4	..	20	22.06	17.25	16.72	5.34	0.00519	0.0934	0.0934 + 0.0096 = 0.1030	14.1	15.4
Second receiver											
4	..	10	11.03	11.30	10.95	0.08	0.00008	0.0008	.. + .. = 0.0008	0.11	..
Loss in weight =0.241 gram											
				Run 2.	*Temperature, 410° C.*		*Flow of nitrogen, 2 litres per hour*				
1	..	25	27.58	23.30	22.58	5.00	0.00485	0.0873	.. + .. = 0.0873	11.9	12.9
2	..	25	27.58	21.00	20.35	7.23	0.00702	0.1264	0.1264 + 0.0048 = 0.1312	17.9	19.5
				Run 3.	*Temperature, 420° C.*		*Flow of nitrogen, 2 litres per hour*				
1	..	25	25.07	..	12.8	12.27	0.0119	0.2142	.. + .. = 0.2142	29.2	31.7
2	..	25	25.07	..	4.2	20.87	0.0202	0.3636	0.3636 + 0.0119 = 0.3755	51.1	55.6
3	..	30	30.09	..	5.3	24.79	0.0240	0.4320	0.4320 + 0.0321 = 0.4641	63.1	68.7
4	..	35	35.1	..	9.0	26.1	0.0253	0.4554	0.4554 + 0.0561 = 0.5115	69.7	74.9
5	..	35	35.1	..	8.3	26.8	0.0260	0.4680	0.4680 + 0.0814 = 0.5494	74.5	81.3
6	..	35	35.1	..	9.2	25.9	0.0251	0.4518	0.4518 + 0.1074 = 0.5592	76.1	83.2
8	..	35	35.1	..	8.8	26.3	0.0255	0.4590	0.4590 + 0.1325 = 0.5915	80.5	88.0
12	..	35	35.1	..	15.5	19.6	0.0190	0.3420	0.3420 + 0.2473 = 0.5893	80.3	88.3
Second receiver											
12	..	10	10.0	..	9.2	0.8	0.00076	0.0076	.. + .. = 0.0076	1.03	..
Loss in weight =0.756 gram. Conditions: KOH in receivers; O_2 removed and gas dried											
				Run 4.	*Varying Temperature.*		*Flow of nitrogen, 2 litres per hour*				
1	180	10	10.76	10.95	10.61	0.15	0.00015	0.0026	.. + .. = 0.0026	0.36	0.39
2	200	10	10.76	10.95	10.61	0.15	0.00015	0.0026	0.0026 + 0.0001 = 0.0027	0.37	0.40
3	250	10	10.76	10.90	10.56	0.20	0.00019	0.0035	0.0035 + 0.0003 = 0.0038	0.52	0.57
4	300	15	16.14	16.30	15.79	0.35	0.00034	0.0061	0.0061 + 0.0005 = 0.0066	0.90	0.98
5	350	15	16.14	16.20	15.70	0.44	0.00043	0.0077	0.0077 + 0.0008 = 0.0085	1.16	1.26
6	400	25	26.90	22.50	21.80	5.10	0.00495	0.0891	0.0891 + 0.0013 = 0.0904	12.3	13.4
7	410	25	26.90	14.05	13.61	13.29	0.0129	0.2322	0.2322 + 0.0062 = 0.2384	32.5	35.3
8	420	35	37.66	11.60	11.24	26.42	0.0257	0.4626	0.4626 + 0.0191 = 0.4817	65.5	71.3
9	430	50	53.80	24.45	23.69	30.11	0.0292	0.5256	0.5256 + 0.0448 = 0.5704	77.7	84.6
10	440	50	53.80	21.70	21.03	32.77	0.0318	0.5724	0.5724 + 0.0740 = 0.6464	88.0	96.0
11	450	50	53.80	22.70	22.00	31.80	0.0309	0.5562	0.5562 + 0.1058 = 0.6620	90.6	99.0
Second receiver											
11	.	10	10.76	10.70	10.36	0.40	0.00039	0.0039	.. + .. = 0.0039	0.53	..
Loss in weight =0.809 gram											

SERIES II

Total hours	Iodine added Cc.	Equivalent 0.1 *N* iodine Cc.	Thio required Cc.	0.1 *N* thio required Cc.	0.1 *N* iodine taken up Cc.	Acetone in sample Grams	Acetone in first receiver Grams	Total yield acetone Grams					Apparent yield Per cent.	True yield from actual acetate in charge Per cent.
				Run 5.	*Temperature, 430° C.*		*Flow of nitrogen, 0.5 litre per hour*							
1	25	24.96	..	6.4	18.56	0.0180	0.3040	..		..		0.3040	41.4	45.0
2	35	34.95	..	8.5	26.45	0.0257	0.4626	0.4626	+	0.0180	=	0.4806	65.4	71.0
3	35	34.95	..	7.3	27.65	0.0268	0.4824	0.4824	+	0.0437	=	0.5261	71.6	77.8
5	35	34.95	..	8.3	26.65	0.0258	0.4644	0.4644	+	0.0974	=	0.5618	76.5	83.2
7	35	34.95	..	9.5	25.45	0.0247	0.4446	0.4446	+	0.1485	=	0.5931	80.8	87.9
9	35	34.95	..	12.0	22.95	0.0223	0.4014	0.4014	+	0.1979	=	0.5993	81.7	88.8
Second receiver—one titration, no acetone present														
Loss in weight =0.748 gram. CO_2 equivalent to CaO present =4.4 mg. Loss in weight $-CO_2$ equivalent =0.743 gram														
				Run 6.	*Temperature, 430° C.*		*Flow of nitrogen, 1.5 litres per hour*							
1	30	29.96	..	5.8	24.16	0.0234	0.4212	..		..		0.4212	57.3	62.3
2	35	34.95	..	7.5	27.45	0.0266	0.4788	0.4788	+	0.0234	=	0.5022	68.4	74.5
5	35	34.95	..	9.8	25.15	0.0244	0.4392	0.4392	+	0.1014	=	0.5406	73.6	80.5
8	35	34.95	..	12.5	22.45	0.0128	0.3924	0.3924	+	0.1718	=	0.5642	76.8	83.9
12	35	34.95	..	15.3	19.65	0.0191	0.3438	0.3438	+	0.2350	=	0.5788	78.85	86.4
Second receiver														
12	10	9.98	..	9.5	0.48	0.00047	0.0047	..		..		0.0047	0.6	..
Loss in weight =0.715 gram. CO_2 equivalent to CaO present =4.4 mg.														

SERIES III

Run 7. Temperature, 430° C. Flow of nitrogen, 2 litres per hour

(Charge subjected to 430° C. for 30 minutes before starting current of nitrogen)

1	35	35.63	17.50	16.98	18.65	0.0181	0.3258	..	..		0.3258	44.4	48.2
2	35	35.63	7.40	7.18	28.45	0.0276	0.4968	0.4968	+ 0.0181	=	0.5149	70.1	76.3
3	35	35.63	4.25	4.12	31.51	0.0306	0.5508	0.5508	+ 0.0457	=	0.5965	81.4	83.6
5	35	35.63	6.95	6.74	28.89	0.0280	0.5040	0.5040	+ 0.1057	=	0.6097	83.0	90.5
7	35	35.63	9.45	9.17	26.46	0.0256	0.4608	0.4608	+ 0.1706	=	0.6314	86.0	93.9
Second receiver													
7	10	10.18	10.15	9.85	0.33	0.00032	0.0032	..	..		0.0032	0.44	..

Loss in weight = 0.797 gram

Run 8. Temperature, 450° C. Flow of nitrogen, 2 litres per hour

1	50	50.65	17.00	16.58	34.07	0.0331	0.5958	..	..		0.5958	81.2	88.4
2	50	50.65	18.75	18.28	32.37	0.0314	0.5652	0.5652	+ 0.0331	=	0.5983	81.5	88.8
3	50	50.65	20.20	19.70	30.95	0.0301	0.5418	0.5418	+ 0.0645	=	0.6063	82.6	90.0
7	35	35.45	11.30	11.02	24.43	0.0237	0.4266	0.4266	+ 0.1730	=	0.5996	81.6	89.3
Second receiver													
7	15	15.20	15.15	14.77	0.43	0.00042	0.0042	..	..		0.0042	0.57	..

Loss in weight = 0.782 gram

Run 9. Temperature, 450° C. Flow of nitrogen, 2 litres per hour

(Charge kept at 450° C. for 30 minutes before gas stream was started)

1	50	50.00	26.80	26.13	23.87	0.0232	0.4076	..	..		0.4076	55.5	60.4
2	50	50.00	23.50	22.91	27.09	0.0261	0.4698	0.4698	+ 0.0232	=	0.4930	67.2	73.2
3	35	35.00	7.40	7.21	27.79	0.0270	0.4860	0.4860	+ 0.0493	=	0.5353	73.0	79.5
7	35	35.00	12.70	12.38	22.62	0.0219	0.3942	0.3942	+ 0.1453	=	0.5425	73.8	80.5
Second receiver													
7	10	10.00	10.00	9.75	0.25	0.00024	0.0024	..	..		0.0024	0.33	..

Loss in weight = 0.704 gram

Run 10. Temperature, 490° C. Flow of nitrogen, 2 litres per hour

(Charge subjected to 490° C. for 30 minutes before starting current of nitrogen)

1	35	35.63	6.35	6.09	29.54	0.0287	0.5166	..	..		0.5166	70.4	76.5
2	50	50.90	23.40	22.44	28.46	0.0276	0.4968	0.4968	+ 0.0287	=	0.5255	71.6	78.0
3	50	50.90	23.90	22.92	27.98	0.0271	0.4878	0.4878	+ 0.0563	=	0.5441	74.0	80.6
7	35	35.63	13.25	12.71	22.82	0.0222	0.3996	0.3996	+ 0.1571	=	0.5567	75.8	83.0
Second receiver													
7	10	10.18	10.35	9.93	0.45	0.00044	0.0044	..	..		0.0044	0.60	..

Run 11. Temperature, 430° C. Flow of carbon dioxide, 2 litres per hour

(Gas stream not started till temperature was in neighbourhood of 400° C.)

1	35	35.10	5.5	5.5	29.6	0.0287	0.5166	..	..		0.5166	70.3	76.5
2	35	35.1	2.4	2.4	32.7	0.0137	0.5706	0.5706	+ 0.0287	=	0.5393	73.4	80.0
3	40	40.12	8.0	8.0	32.12	0.0311	0.5298	0.5298	+ 0.0604	=	0.6202	84.5	92.1
7	35	35.1	9.5	9.5	25.6	0.0248	0.4464	0.4464	+ 0.1752	=	0.6216	84.7	92.7
9	35	35.1	11.9	11.9	23.2	0.0225	0.4050	0.4050	+ 0.2236	=	0.6286	85.6	93.8
Second receiver													
9	10	10.03	9.5	9.5	0.53	0.00051	0.0051	..	..		0.0051	0.7	..

Loss in weight = 0.794 gram

SERIES IV

Total hours	Iodine added Cc.	Equivalent 0.1 *N* iodine Cc.	Thio required Cc.	0.1 *N* thio required Cc.	0.1 *N* iodine taken up Cc.	Acetone in sample Grams	Acetone in first receiver Grams	Total yield acetone Grams	Apparent yield Per cent.	True yield from actual acetate in charge Per cent.
				Run 12. Temperature, 430° C. Flow of air, 2 litres per hour						
1	35	37.66	12.80	12.40	25.26	0.0245	0.4410	.. + .. = 0.4410	60.1	65.3
4	35	37.66	16.55	16.04	21.62	0.0210	0.3780	0.3780 + 0.0703 = 0.4483	61.2	66.8
Second receiver										
4	10	10.70	10.90	10.56	0.14	0.00014	0.0014	.. .. 0.0014	0.19	..
Loss in weight =0.795 gram										
				Run 13. Temperature, 450° C. Flow of air, 2 liters per hour						
1	35	37.66	13.30	12.89	24.77	0.0240	0.4320	.. .. 0.4320	58.9	64.0
2	35	37.66	14.65	14.20	23.46	0.0228	0.4104	0.4104 + 0.0240 = 0.4344	59.2	64.3
3	35	37.66	16.50	15.98	21.68	0.0211	0.3798	0.3798 + 0.0468 = 0.4266	58.2	63.3
No second receiver. Loss in weight =0.734 gram										
				Run 14. Temperature, 450° C. Flow of air, 2 litres per hour						
1	35	37.66	12.10	11.72	25.94	0.0251	0.4518	.. .. 0.4518	61.5	67.1
2	35	37.66	13.40	12.98	24.68	0.0239	0.4302	0.4302 + 0.0251 = 0.4553	62.1	68.0
Second receiver										
2	10	10.76	10.70	10.36	0.34	0.00033	0.0033	.. .. 0.0033	0.45	..
Loss in weight =0.795 gram										
				Run 15. Temperature, 490° C. Flow of air, 2 litres per hour						
1	35	35.63	12.10	11.60	24.03	0.0231	0.4158	.. .. 0.4158	56.8	61.7
4	35	35.63	15.60	14.96	20.67	0.0201	0.3618	0.3618 + 0.0660 = 0.4284	58.4	63.7
6	25	25.45	7.40	7.10	18.35	0.0178	0.3204	0.3204 + 0.1054 = 0.4258	58.0	63.5
Second receiver										
6	10	10.18	10.30	9.88	0.30	0.00029	0.0029	.. .. 0.0029	0.40	..
Loss in weight =0.791 gram										

SERIES V

Run 16. Temperature, 450° C. Flow of nitrogen, 2 litres per hour

(0.5 gram "ferrum redactum" mixed with charge)

1	50	50.00	14.95	14.58	35.42	0.0344	0.6192	..		..		0.6192	84.4	91.8
4	50	50.00	18.95	18.48	31.52	0.0306	0.5508	0.5508	+	0.1028	=	0.6536	89.0	97.1
7	35	35.00	8.90	8.68	26.32	0.0255	0.4590	0.4590	+	0.1897	=	0.6487	88.4	96.8
Second receiver														
7	10	10.00	9.75	9.51	0.49	0.00048	0.0048	..		..		0.0048	0.66	..

Loss in weight =0.796 gram

Run 17. Temperature, 450° C. Flow of nitrogen, 2 litres per hour

(0.5 gram "ferrum redactum" added and charge subjected to 450° C. for 30 minutes before starting the current of nitrogen)

1	35	35.63	13.40	13.00	22.63	0.0220	0.3960	..		..		0.3960	54.0	58.7
2	35	35.63	4.65	4.51	31.12	0.0302	0.5436	0.5436	+	0.0220	=	0.5656	77.0	83.7
5	35	35.63	8.90	8.63	27.00	0.0262	0.4716	0.4716	+	0.1089	=	0.5805	79.0	85.9

No second receiver. Loss in weight =0.745 gram

Run 18. Temperature, 450° C. Flow of nitrogen, 2 litres per hour

(0.5 gram powdered reduced copper mixed with charge)

1	50	50.00	14.50	14.14	38.86	0.0348	0.6264	..		..		0.6264	85.4	92.9
2	50	50.00	14.80	14.43	35.57	0.0345	0.6210	0.6210	+	0.0348	=	0.6558	89.5	97.5
5	50	50.00	20.40	19.89	30.11	0.0292	0.5256	0.5256	+	0.1327	=	0.6583	89.6	97.9
7	35	35.00	8.50	8.29	26.71	0.0259	0.4662	0.4662	+	0.1900	=	0.6562	89.5	98.0
Second receiver														
7	10	10.00	9.80	9.55	0.45	0.00044	0.0044	..		..		0.0044	0.60	..

Loss in weight =0.794 gram

SERIES VI

				Run 19.	*Temperature, 430° C.*	*Flow of nitrogen, 2 litres per hour*							
1	50	50.90	21.50	20.85	30.05	0.0292	0.5256	..		..	=	0.5256	71.5	77.8
2	50	50.90	19 45	18.87	32.03	0.0311	0.5598	0.5598	+	0.0292	=	0.5890	80.2	87.4
3	50	50.90	19.40	18.82	32.08	0.0312	0.5616	0.5616	+	0.0603	=	0.6219	84.7	92.3
6	35	35.63	8.30	8.05	27.58	0.0267	0.4806	0.4806	+	0.1488	=	0.6294	85.6	93.7
Second receiver														
6	10	10.18	10.00	9.70	0.48	0.00047	0.0047	..		..		0.0047	0.64	..
Loss in weight =0.792 gram														
				Run 20.	*Temperature, 450° C.*	*Flow of nitrogen, 2 litres per hour*							
1	50	50.65	13.25	12.92	37.73	0.0366	0.6588	..		..		0.6588	89.4	97.3
2	50	50.65	15.05	14.67	35.98	0.0349	0.6282	0.6282	+	0.0366	=	0.6648	90.5	98.6
3	50	50.65	16.90	16.48	34.17	0.0331	0.5958	0.5958	+	0.0715	=	0.6673	91.0	99.3
4	50	50.65	19.00	18.52	32.13	0.0312	0.5616	0.5616	+	0.1046	=	0.6662	90.8	99.2
5	50	50.65	21.00	20.47	30.18	0.0293	0.5274	0.5274	+	0.1358	=	0.6632	90.4	98.9
6	50	50.65	22.65	22.08	28.57	0.0277	0.4986	0.4986	+	0.1657	=	0.6637	90.4	99.0
7	50	50.65	24.25	23.64	27.01	0.0263	0.4734	0.4734	+	0.1928	=	0.6662	90.8	99.5
Second receiver														
7	10	10.13	9.80	9.55	0.56	0.00054	0.0054	..		..		0.0054	0.74	..
Loss in weight =0.800 gram														
				Run 21.	*Temperature, 450° C.*	*Flow of nitrogen, 2 litres per hour*							
1	50	48.6	10.85	10.58	37.02	0.0359	0.6472	..		..		0.6472	88.0	95.7
2	50	48.6	13.20	12.86	35.74	0.0347	0.6156	0.6156	+	0.0359	=	0.6515	88.7	96.6
3	50	48.6	14.65	14.28	34.32	0.0333	0.5994	0.5994	+	0.0706	=	0.6700	91.2	99.5
4	50	48.6	16.80	16.38	32.22	0.0313	0.5634	0.5634	+	0.1039	=	0.6673	91.0	99.4
5	50	48.6	17.50	17.06	30.54	0.0296	0.5328	0.5328	+	0.1352	=	0.6680	91.1	99.7
6	50	48.6	20.35	19.84	28.76	0.0279	0.5022	0.5022	+	0.1648	=	0.6670	90.9	99.6
7	50	48.6	22.15	21.60	27.00	0.0262	0.4716	0.4716	+	0.1927	=	0.6643	90.5	99.3
Second receiver														
7	10	9.72	9.3	9.07	0.65	0.00063	0.0063	..		..		0.0063	0.86	..
Loss in weight =0.806 gram														
				Run 22.	*Temperature, 490° C.*	*Flow of nitrogen, 2 litres per hour*							
1	50	50.65	13.70	13.36	37.29	0.0362	0.6516	..		..		0.6516	88.8	96.6
2	50	50.65	15.00	14.62	36.03	0.0349	0.6282	0.6282	+	0.0362	=	0.6644	90.5	98.5
3	50	50.65	17.10	16.67	33.98	0.0330	0.5940	0.5940	+	0.0711	=	0.6651	90.6	98.6
4	50	50.65	19.05	18.57	32.08	0.0311	0.5598	0.5598	+	0.1041	=	0.6639	90.4	98.5
5	50	50.65	20.80	20.28	30.37	0.0295	0.5310	0.5310	+	0.1352	=	0.6662	90.8	98.9
6	50	50.65	22.50	21.94	28.71	0.0278	0.5004	0.5004	+	0.1647	=	0.6651	90.7	98.8
7	35	35.45	8.40	8.19	27.26	0.0264	0.4752	0.4752	+	0.1925	=	0.6677	90.9	99.1
Second receiver														
7	10	9.75	9.80	9.55	0.20	0.00019	0.0019	..		..		0.0019	0.26	..
Loss in weight =0.796 gram														

ON THE MECHANISM OF THE ACTION OF PROMOTERS IN CATALYSIS

By M. C. Boswell, *Professor of Organic Chemistry,*
and C. H. Bayley, *Research Assistant*

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A theory has been developed by the senior author with regard to the mechanism of catalysis by partially reduced oxides and by platinum black.[1] According to this theory the catalyst consists of particles of unreduced oxide surrounded by a layer of reduced metal or lower oxide carrying positively charged hydrogens and negatively charged hydroxyls, and this surface layer of dissociated water molecules is the seat of the

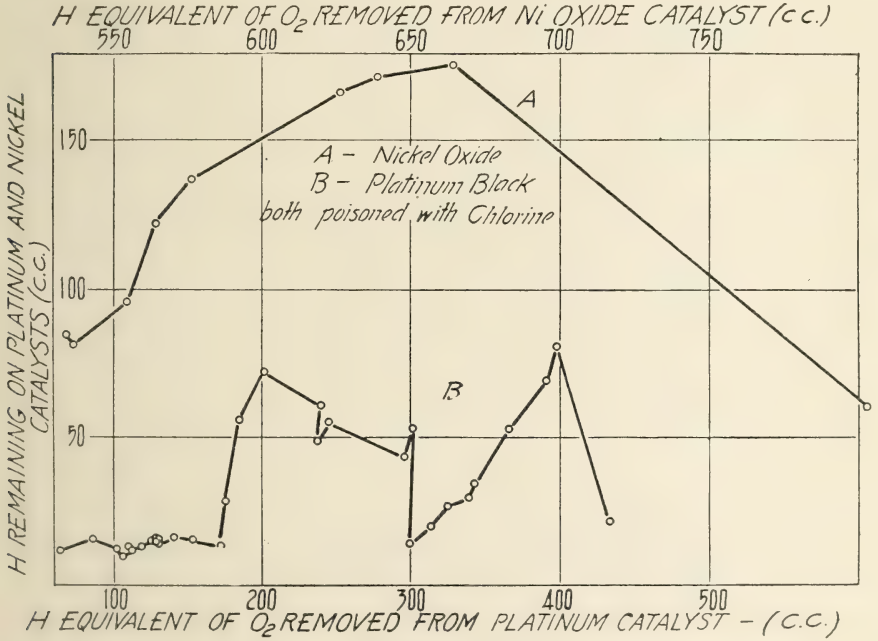

Fig. 1

catalysis of oxidation, of reduction and of hydrolysis observed with these partially reduced oxides. This is clearly seen in Fig. 1 which should be compared with Figs. 2-4.

[1] Boswell: Proc. Roy. Soc. Canada, 16, III (1922); Boswell and McLaughlin: 17, III (1923).

More recently the authors have shown[2] that this theory gives a very satisfactory picture, in harmony with the facts, of the so-called poisoning of catalysts. The poisoning is due to the destruction of the surface film which is the real seat of the catalytic properties. The charged hydrogens and hydroxyls lose their charges and pass off as free water. Thus, the complex loses the very effective protection afforded by this surface for the underlying interior content of oxygen. Accordingly, if the catalyst, in this condition, is brought into contact with free hydrogen, the interior oxygen content of the complex is rapidly removed as water, the poison still present (it has regenerated in a cycle of reactions) preventing the re-establishment of the catalytic film.

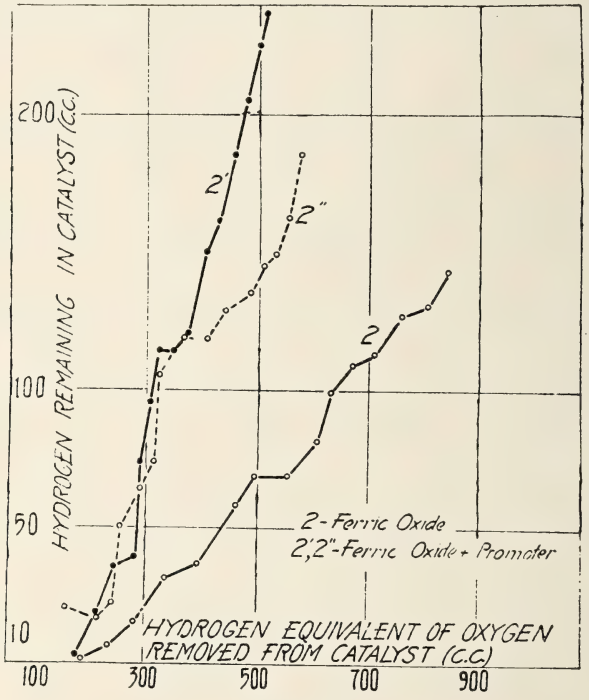

FIG. 2

If this view of the mechanism of the action of catalysts and of catalytic poisons is correct, then the action of the so-called "promoters" in still further enhancing the activity of catalysts, is immediately suggested by the theory. For, if the activity of the catalysts depends on these surface films of dissociated water, and if the poisoning of the catalyst is due to the destruction of these films and the prevention of their

[2]Boswell and Bayley: J. Phys. Chem. 29, 11-19 (1925).

re-formation, then the action of promoters is probably due to the increased concentration of charged hydrogens and hydroxyls in the surface film. That is, the promoter enables the catalyst to hold more charged hydrogens and hydroxyls in the surface films per gram of catalyst than the catalyst alone can hold. Working with the well known cases of promoter action, viz., cerium oxide as promoter of partially reduced ferric oxide and potassium hydroxide as promoter of platinum black, we have found that the above conclusions of the theory are strikingly verified by the facts. Iron oxide was reduced in hydrogen at 275°C. The hydrogen remaining on the catalyst was plotted against oxygen removed from the catalyst as free water.

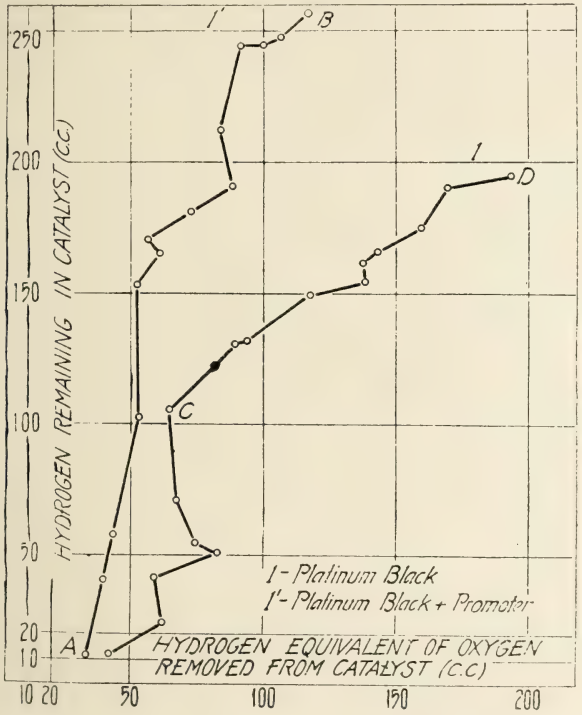

FIG. 3

Curve 2, Fig. 2, represents this action in the case of oxide alone, and curves 2' and 2'' represent the action where 0.5% cerium oxide was present uniformly distributed throughout the iron oxide. It will be seen that the amount of hydrogen remaining on the catalyst for any given amount of oxygen removed, is greater in the presence of the promoter than in its absence. Also that the rate at which oxygen is removed as

free water from the oxide layer is very much slower in the presence of the promoter. That is, in terms of the theory, for any given amount of oxygen removed as water from the catalyst, the catalyst is able to hold a very much greater amount of water as charged hydrogens and hydroxyls on the surface, in the case where the promoter is used. It will also be observed that the general form of the curve indicates that the ratio of hydrogen remaining on the catalyst to oxygen removed from the catalyst is a constant.

Likewise, in the case of platinum black, using potassium hydroxide as promoter (see Fig. 3), the same increased concentration of dissociated

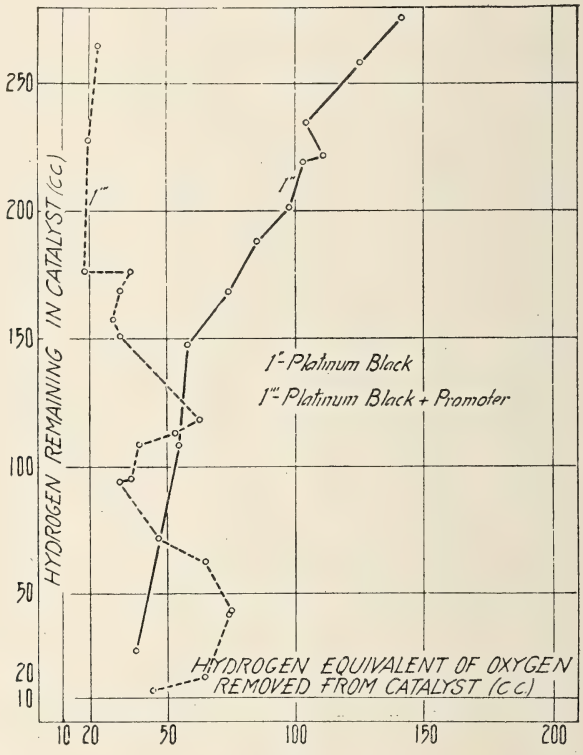

FIG. 4

water in the surface film, and slowness in the loss of interior oxygen is found in the presence of the promoter. In this case, where the promoter is absent, there is a distinct change of direction of the curve at the point C, the general form from C to D being approximately a straight line. That is, at the point C the rate of loss of oxygen is markedly increased and is constant to the point D, whereas where the

promoter is present in the platinum black this sudden break in the curve is not found, the general direction of the curve from A to B being approximately a straight line. That is, the loss of oxygen in the former case, where the promoter was absent, is much greater than when the promoter was present.

Fig. 4 represents the behaviour of platinum black with and without promoter, identical in all respects with the platinum black experiments represented in Fig. 3 with the exception that in the former the platinum black stood in the reaction tubes in an atmosphere of nitrogen for eight weeks. It will be seen that in general the same statements hold in the two cases, and that the action of the promoter is to increase the amount of hydrogen on the catalyst for any given amount of oxygen removed. The chief difference is that in the case of the platinum samples which stood for 8 weeks, the amount of hydrogen remaining on the catalyst for a given amount of oxygen removed is greater than in the freshly prepared platinum, both where the promoter is present and where it is absent. This may possibly be due to the reduction in size of the platinum particles on standing, thus presenting a larger surface and enabling a larger amount of hydrogen and hydroxyl to be held on the surface.

That this hydrogen left on reduced oxide catalysts is present in the form of charged hydrogens and hydroxyls is supported by the experimental evidence already presented in the papers above referred to, and is corroborated by more recent evidence which will be presented by us in the near future. There it will be shown: (1) that the total hydrogen remaining on a partially reduced oxide catalyst is present only to a very slight extent in the form of free dissolved gas; (2) that a large part of this hydrogen is associated with oxygen in an external layer; (3) that the interior content of oxygen is vital for the maintenance of these partially reduced oxides as catalysts; and (4) that platinum black has a large interior oxygen content. This latter fact is of considerable importance to organic chemists who use platinum black as catalyst for hydrogenation. It has been the custom for organic chemists to use platinum black as a hydrogen carrier without regard to the fact that prior oxidation by the high oxygen content of the platinum black may interfere, with the result that, instead of simple hydrogenation, the actions in reality have consisted of oxidation by the platinum black, followed by reduction by hydrogen and further hydrogenation of the reduction product. Pummerer's hydrogenation of rubber[3] using platinum black, as has been shown in this laboratory, falls in this category.

[3]Pummerer: Ber. 55, 3458 (1922).

EXPERIMENTAL

INFLUENCE OF CERIUM OXIDE ON THE REDUCTION OF FERRIC OXIDE

Preparation of Catalyst.

A quantity of Kahlbaum's ferric nitrate crystals were recrystallized from distilled water containing a little nitric acid, to prevent the formation of the basic salt. The crystals were cubical, corresponding to the formula

$$Fe(NO_3)_3 6H_2O.$$

150 grams of the dry crystals were dissolved in 600 cc. water, and the solution divided into 6 portions of 100 cc. each. 5 grams of ceric oxalate were ignited to the oxide and 0.75 gram of this was dissolved in 30 cc. nitric acid (50%). One third of this solution was added to each of three of the ferric nitrate portions—this giving 6 solutions in all—3 containing ferric nitrate alone and 3 containing the ferric and cerium nitrates. The 6 solutions were poured into six 200 cc. crucibles and evaporated to small bulk on the water bath. 2.5 grams of Kahlbaum's C.P. acid washed asbestos were added to the contents of each crucible, and the evaporation carried on to dryness. The residues were ignited simultaneously in an electric muffle at 750°C. The asbestos bearing the oxide was then scraped out and placed into 6 reaction tubes 40 cm. long and 18 mm. in diameter.

Reduction of Catalyst.

The apparatus used was similar to the one used in the previously described papers on platinum and nickel. The apparatus train consisted of a 400 cc. graduated and water jacketted gas burette, two U tubes containing concentrated sulphuric acid on pumice, the reaction tube containing the catalyst, passing through an electric tube furnace, two U tubes containing sulphuric acid on pumice, a small mercury manometer and a 400 cc. gas burette similar to the first one.

The experiments were all run at 275°C. Before the reduction was begun the catalyst tube was thoroughly dried out. This was done by passing nitrogen free from oxygen through the tube heated to 275°C. until no further increase in weight was noticed in the U tube immediately following the catalyst tube.

The method of carrying out the reduction was as follows:

Nitrogen free from oxygen was passed through the train of tubes and through the catalyst tube for half an hour, in order to expel any air

present. The apparatus was now closed and hydrogen introduced into the right hand burette. It was then brought to atmospheric pressure by means of a levelling tube and the volume read. It was then passed over the catalyst and back into the burette, the volume being read after each passage, and the passage being repeated until there was no further

TABLE I

Iron Oxide without Promoter. Fig. 2

Treatment	Hydrogen used up cc.	Hydrogen equivalent of water formed cc.	Hydrogen equivalent of oxygen removed cc.	Hydrogen remaining on catalyst cc.
1	182.9	180.9	180.9	2.0
*—	—	2.0	182.9	0.0
2	55.5	47.9	230.8	7.6
—	—	2.4	233.2	5.2
3	55.5	44.7	277.9	16.0
—	—	1.2	279.1	14.8
4	70.0	52.4	331.5	32.4
—	—	4.8	336.3	27.6
5	69.1	59.3	395.6	37.4
—	—	5.3	400.9	32.1
6	79.2	53.3	454.2	58.0
—	—	0.3	454.5	57.7
7	49.1	38.2	492.7	68.6
—	—	8.9	501.6	59.7
8	59.2	50.3	551.9	68.6
—	—	0.0	551.9	68.6
9	64.6	50.5	602.4	82.7
—	—	0.8	603.2	81.9
10	45.5	28.6	631.8	98.8
—	—	1.7	633.5	97.1
11	50.0	38.0	671.5	109.1
—	—	4.8	676.3	104.3
12	41.8	32.3	708.6	113.8
—	—	1.3	709.9	112.5
13	59.1	44.1	754.0	127.5
—	—	2.7	756.7	124.8
14	53.7	47.8	804.5	130.7
—	—	1.4	805.9	129.3
15	61.0	36.4	842.3	153.9

*After standing over night in nitrogen, nitrogen was passed and the temperature raised to 275°C. and maintained at this temperature for a quarter of an hour, and the water weighed.

diminution in volume. Nitrogen free from oxygen was now passed through the apparatus for half an hour in order to expel all the free hydrogen (it has been shown that no hydrogen is removed from the catalyst during this process). The catalyst tube was now closed at both ends and the water absorption tubes disconnected and weighed in order to determine the water formed during the reduction. The catalyst tube

TABLE II

Iron Oxide with Promoter. Fig. 2

Treatment	Hydrogen used up cc.	Hydrogen equivalent of water formed cc.	Hydrogen equivalent of oxygen removed cc.	Hydrogen remaining on catalyst cc.
1	175.6	155.1	155.1	20.5
*—	—	5.0	160.1	15.5
2	49.1	47.5	207.6	17.1
—	—	2.1	209.7	15.0
3	41.9	34.1	243.8	22.8
—	—	3.1	246.9	19.7
4	34.6	4.2	251.1	50.1
—	—	1.2	252.3	48.9
5	45.5	30.8	283.1	63.6
—	—	0.0	283.1	63.6
6	40.0	30.1	313.2	73.5
—	—	4.8	318.0	68.7
7	39.1	2.8	320.8	105.0
—	—	5.6	326.4	99.4
8	58.2	38.5	364.9	119.1
—	—	5.6	370.5	113.5
9	41.0	36.4	406.9	118.1
—	—	5.7	412.6	112.4
10	46.4	29.8	442.4	129.0
—	—	6.0	448.4	123.0
11	47.3	35.3	483.7	135.0
—	—	0.2	483.9	134.8
12	32.8	22.2	506.1	145.4
—	—	2.6	508.7	142.8
13	30.9	23.9	532.6	149.8
—	—	1.6	534.2	148.2
14	33.7	19.1	553.3	162.8
—	—	0.0	553.3	162.8
15	46.4	22.5	575.8	186.7

*After standing over night in nitrogen, nitrogen was passed and the temperature raised to 275°C. and maintained at this temperature for a quarter of an hour, and the water weighed.

TABLE III

Iron Oxide with Promoter. Fig. 2

Treatment	Hydrogen used up cc.	Hydrogen equivalent of water formed cc.	Hydrogen equivalent of oxygen removed cc.	Hydrogen remaining on catalyst cc.
1	175.6	171.6	171.6	4.0
*—	—	3.8	175.4	0.2
2	59.1	39.5	214.9	19.8
—	—	5.0	219.9	14.8
3	43.7	21.5	241.4	37.0
—	—	5.3	246.7	31.7
4	38.2	31.1	277.8	38.8
—	—	1.4	279.2	37.4
5	42.8	6.6	285.8	73.6
—	—	2.2	288.0	71.4
6	37.3	12.8	300.8	95.9
—	—	3.4	304.2	92.5
7	39.1	16.0	320.2	115.6
—	—	6.2	326.4	109.4
8	25.5	20.4	346.8	114.5
—	—	2.6	349.4	111.9
9	29.1	20.9	370.3	120.1
—	—	2.5	372.8	117.6
10	65.5	32.3	405.1	150.8
—	—	1.7	406.8	149.1
11	31.8	18.8	425.6	162.1
—	—	1.1	426.7	161.0
12	51.9	26.7	453.4	186.2
—	—	0.0	453.4	186.2
13	44.6	25.2	478.6	205.6
—	—	0.6	479.2	205.0
14	42.8	22.4	501.6	225.4
—	—	0.1	501.7	225.3
15	26.4	13.7	515.4	238.0

was again connected to the nitrogen supply and allowed to cool in a current of nitrogen. It was securely closed and allowed to remain over night in an atmosphere of nitrogen. Next morning the water absorption tubes were inserted and nitrogen passed at 275°C. for fifteen minutes in order to sweep over the water formed over night, which was then weighed. The cycle of operations was now repeated.

Tables I-III show the results of the measurements.

*After standing over night in nitrogen, nitrogen was passed and the temperature raised to 275°C. and maintained at this temperature for a quarter of an hour, and the water weighed.

INFLUENCE OF POTASSIUM HYDROXIDE ON THE REDUCTION OF PLATINUM BLACK

The eight grams of platinum black used in these experiments were prepared by a modification of the method of Loew[1] and described in the above-mentioned paper on the "Mechanism of Catalysis by Platinum".[2]

2 grams of this platinum black were used in each experiment. This was placed in a porcelain boat 7 cm. × 8 mm. and heated to 150°C. in a tube of Jena glass 40 cm. × 18 mm. until there was no further increase in the weight of the U tube—indicating that no more water was being evolved.

Platinum Black without Promoter.

2 grams of the platinum black were dried at 150°C. to constant weight and treated alternately with hydrogen and oxygen in the same apparatus as used in the experiments with ferric oxide.

Table IV gives the measurements obtained.

TABLE IV

Platinum Black without Promoter. Fig. 3

Treatment	Hydrogen used up cc.	Oxygen used up cc.	Hydrogen equivalent of water formed cc.	Hydrogen equivalent of oxygen removed cc.	Hydrogen remaining on catalyst cc.
1	54.6	—	42.0	42.0	12.6
	—	0	2.8	44.8	—
2	35.5	—	18.8	63.6	26.5
	—	11.8	1.2	41.2	—
3	32.8	—	17.3	58.5	40.8
	—	0	4.2	62.7	—
4	34.6	—	20.1	82.8	51.1
	—	11.8	0.7	59.9	—
5	20.0	—	14.2	74.1	56.2
	—	11.8	2.4	52.9	—
6	31.8	—	14.5	67.4	71.1
	—	8.1	3.0	54.2	—
7	48.2	—	9.9	64.1	106.4
	—	3.6	3.7	60.6	—
8	55.5	—	27.7	88.3	130.5
	—	4.5	1.2	80.5	—
9	15.5	—	13.0	93.5	131.8
	—	4.5	5.0	89.5	—
10	51.0	—	28.1	117.6	149.7
	—	0	1.2	118 8	—

[1]Loew: Ber. 23, 289 (1890).

[2]Proc. Roy. Soc. Canada, 16, III (1922).

TABLE IV—*Cont.*

11	26.3	—	19.9	138.7	154.9
	—	10.0	3.3	122.0	—
12	26.4	—	16.0	138.0	162.0
	—	7.3	1.4	124.8	—
13	25.5	—	18.7	143.5	167.4
	—	0	1.4	144.9	—
14	24.5	—	14.8	159.7	175.7
	—	5.6	2.7	151.2	—
15	35.5	—	17.6	168.8	190.9
	—	0	2.2	171.0	—
16	19.1	—	12.4	183.4	195.4

TABLE V

Platinum Black with Promoter. Fig. 3

Treatment	Hydrogen used up cc.	Oxygen used up cc.	Hydrogen equivalent of water formed cc.	Hydrogen equivalent of oxygen removed cc.	Hydrogen remaining on catalyst cc.
1	45.5	—	33.7	33.7	11.8
	—	6.4	0.8	21.7	
2	48.2	—	17.9	39.6	41.3
	—	6.4	2.3	29.1	
3	33.7	—	14.0	43.1	58.7
	—	6.4	0.0	30.3	
4	67.3	—	23.0	53.3	103.0
	—	16.4	1.3	21.8	
5	82.0	—	29.7	51.5	154.0
	—	6.4	0.4	39.1	
6	34.6	—	21.6	60.7	166.6
	—	12.7	3.1	38.4	
7	26.3	—	18.5	56.9	171.3
	—	6.4	0.0	44.1	
8	12.8	—	12.8	56.9	171.3
	—	4.5	0.0	47.9	
9	33.7	—	24.2	72.1	180.8
	—	2.7	0.0	66.7	
10	30.9	—	21.6	88.3	190.1
	—	8.2	1.5	73.4	
11	36.4	—	10 8	84.2	214.2
	—	3.6	1.1	78.1	
12	46.4	—	13.5	91.6	246.0
	—	4.5	1.9	84.5	
13	16.5	—	15.2	99.7	245.4
	—	2.7	1.5	95.8	
14	15.5	—	11.2	107.0	248.2
	—	3.6	4.0	103.8	
15	27.3	—	13.4	117.2	258.1

TABLE VI

Platinum Black which stood in Nitrogen for eight weeks. Fig. 4
The following measurements were obtained:

Treatment	Hydrogen used up cc.	Oxygen used up cc.	Hydrogen equivalent of water formed cc.	Hydrogen equivalent of oxygen removed cc.	Hydrogen remaining on catalyst cc.
1	65.5	—	37.0	370	28.5
	—	2.7	3.1	34.7	25.4
2	101.9	—	19.3	54.0	108.0
	—	5.5	4.0	47.0	104.0
3	54.6	—	11.1	58.1	147.5
	—	1.8	0.4	54.9	147.1
4	40.9	—	19.4	74.3	168.6
	—	3.6	3.0	70.1	165.6
5	36.4	—	14.5	84.6	187.5
	—	4.5	4.0	79.6	183.5
6	35.5	—	17.3	96.9	201.7
	—	3.6	0.0	89.7	201.7
7	30.9	—	13.4	103.1	219.2
	—	2.7	0.0	97.7	219.2
8	15.5	—	13.5	111.2	221.2
	—	10.0	0.0	91.2	221.2
9	26.4	—	13.4	104.6	234.2
	—	4.5	2.2	97.8	232.0
10	54.6	—	28.8	126.6	257.8
	—	3.6	0.0	119.4	257.8
11	41.0	—	22.1	141.5	276.7

Platinum Black with Promoter.

To the 2 grams of platinum black contained in the boat were added 2 cc. of N/10 KOH solution. The amount of KOH added was, therefore, approximately 0.5% of the weight of platinum. The boat was heated to 125°C. in a stream of nitrogen until no more water was evolved. The temperature was then raised to 150°C. and nitrogen passed at this temperature until no more moisture was evolved. The data are given in Tables V-VII.

The question naturally arises, why do these promoters cause this large increase in concentration of dissociated water in the surface films of the catalysts. Aluminum oxide and cerium oxide, when heated to temperatures up to 450°C., have a capacity of holding very considerable amounts of water on their surfaces. Likewise the alkali hydroxides lose all their water only at very high temperatures. It seems, then, that at the temperatures at which iron oxide is used as a catalyst (around 550° C. in

TABLE VII

Platinum Black which stood in Nitrogen for eight weeks and Promoter added as in previous set of platinum experiments. Fig. 4

Treatment	Hydrogen used up cc.	Oxygen used up cc.	Hydrogen equivalent of water formed cc.	Hydrogen equivalent of oxygen removed cc.	Hydrogen remaining on catalyst cc.
1	58.0	—	44.5	44.5	13.5
	—	0.0	0.0	44.5	13.5
2	24.6	—	20.5	65.0	17.6
	—	6.4	1.7	53.9	15.9
3	49.1	—	20.4	74.3	44.6
	—	9.4	3.8	59.3	40.8
4	16.8	—	14.8	74.1	42.8
	—	19.1	3.4	39.3	39.4
5	49.1	—	26.1	65.4	62.4
	—	20.9	4.8	28.4	57.6
6	32.8	—	18.7	47.1	71.7
	—	19.1	2.4	11.3	69.3
7	44.6	—	20.1	31.4	93.8
	—	6.4	0.0	18.6	93.8
8	17.3	—	16.9	35.5	94.2
	—	7.3	0.0	20.9	94.2
9	32.8	—	18.3	39.2	108.7
	—	4.6	1.2	31.2	107.5
10	28.2	—	21.9	53.1	113.8
	—	5.5	4.2	46.3	109.6
11	25.5	—	16.2	62.5	118.9
	—	27.3	1.3	9.2	117.6
12	58.8	—	22.8	32.0	150.4
	—	10.0	1.6	13.6	148.8
13	23.7	—	14.9	28.5	157.6
	—	7.3	0.0	13.9	157.6
14	30.0	—	18.4	32.3	169.2
	—	5.5	1.2	22.5	168.0
15	21.8	—	13.6	36.1	176.2
	—	19.1	5.0	2.9	171.2
16	19.1	—	14.7	17.6	175.6
	—	5.5	2.5	9.1	173.1
17	64.6	—	10.6	19.7	227.1
	—	6.4	2.4	9.3	224.7
18	54.6	—	13.4	22.7	265.9

the ammonia synthesis) and the temperature at which nickel oxide is used as a catalyst (around 150°C. in hydrogenations) and the temperature at which platinum black is used as a catalyst (around 450°C. in

the ammonia synthesis), the particles of aluminum oxide, cerium oxide and potassium hydroxide disseminated throughout the catalysts hold the charged hydrogens and hydroxyls in larger concentration in the reduced layer surrounding the catalyst. Another and perhaps more important reason for this enhanced capacity for holding dissociated water in the reduced layer, is to be found in the fact that in the presence of the promoter a transfer is more quickly made of oxygen from the interior of the catalyst to the surface layer.

Thus, the promoter probably exerts its influence: (1) by enabling the catalytic surface film to form more rapidly on reduction in hydrogen; (2) by acting as particles scattered through the reduced layer, around which dissociated water can accumulate at higher concentrations; (3) by increasing the stability of the catalytic film so that it is not lost, at elevated temperatures, as free water.

In connection with the general theory of catalysis developed in this laboratory it may be pointed out that just as metallic oxides and platinum black upon reduction at low temperatures yield complexes having a high hydrogen content (which hydrogen we believe is present in the form of charged hydrogens and hydroxyls constituting the surface film, which is responsible for the catalytic properties of these catalysts) so it has been found in this laboratory that some chlorides, nitrides and sulphides, upon reduction in hydrogen at low temperatures, likewise form complexes containing a relatively large amount of hydrogen in some special form, probably in a form analogous to the charged hydrogens and hydroxyls in the case of partially reduced oxides. This is indicated by the fact that these complexes formed from nitrides, chlorides and sulphides also possess the catalytic properties one would expect to find in complexes having surface films of analogous constitutions. The facts and arguments will be presented in detail in the near future.

SUMMARY

The theory of catalytic action by partially reduced oxides and by platinum black and of the mechanism of the action of catalytic poisons of these catalysts developed in this laboratory, is here expanded to include the mechanism of promoter action.

It has been shown that the theory indicates that the probable function of promoters is to increase the concentration of charged hydrogens and hydroxyls in the catalytic surface layer. The experimental data are entirely in harmony with this theory.

An explanation of the inner mechanism of this process is suggested.

Nitrides, chlorides and sulphides, on reduction in hydrogen form complexes having relatively large amounts of hydrogen remaining on them and having the catalytic properties indicated by the general theory of catalysis developed in this laboratory.

Note. The following corrections should be made in the paper of Boswell and Bayley: J. Phys. Chem. 29, II (1925).

page 14 line 7 for .0001 read .01
page 14 line 8 for 33.0 read 24.5
page 14 line 10 for 173.9 read 174.9
page 14 line 35 for 173.9 read 174.9

In the experiment recorded on page eighteen, 0.0164 gram of water was given off during the intermediate passage of nitrogen after the ninth passage of oxygen (line 18) and before the tenth passage of hydrogen (line 19). This measurement was taken into account in the calculation, although it was omitted in the table.

ON THE MECHANISM OF CATALYSIS BY ALUMINIUM OXIDE

By M. C. Boswell, *Professor of Organic Chemistry*, and H. M. Dilworth, *Research Assistant*

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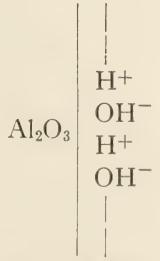
Experimental evidence and arguments have been presented by the senior author and his students, which lend considerable support to the theory that platinum black and partially reduced oxides function as catalysts by means of surface films of dissociated water, *i.e.*, positively charged hydrogens and negatively charged hydroxyls.[1]

It seemed probable that the origin of the catalytic properties of aluminium oxide might likewise be found in a similar film on the aluminium oxide particles. Accordingly the quantitative experiments recorded in this paper were undertaken, with a view to determining whether this hypothesis appeared to be in harmony or not with the facts.

It was recognized at the outset that aluminium oxide differs markedly in constitution from partially reduced oxides. In the case of the latter, as has been pointed out in the above papers, there is an interior oxygen content which can be drawn upon either for the maintenance of the surface film on the particles, or for oxidation purposes directly if the surface film is destroyed. However, in the case of aluminium oxide, although there is a large interior content of oxygen, this is not, owing to the great stability of the oxide, available for any such purposes as those indicated above in the case of reducible oxides. Thus, if a surface layer of charged hydrogens and hydroxyls does exist on the particles of an aluminium oxide catalyst, it is not present in a reduced metal layer superposed on an underlying oxide layer, as in the case of partially reduced oxides, but must constitute a surface layer held in the exterior surface of the particles, thus:



[1] Boswell, Trans. Roy. Soc. Canada, *16* III, 1 (1922); Boswell and McLaughlin, *17* III, 1 (1923); Boswell and Bayley, J. Phys. Chem. *29*, 11, 679 (1925).

The charged hydrogens and hydroxyls constituting the surface film would be in a state of tension due to the mutual attraction of opposite charges. The stability of this film, which will be shown presently, is probably due to this tension. Likewise the remarkable protection afforded by this film for the underlying interior oxygen in the case of partially reduced oxides, may be ascribed to this same tension in the surface film. Indeed the experimental observation of the extreme difficulty of removing all the water from glass surfaces (high temperatures in a vacuum being necessary) is probably connected with the existence of this film of charged hydrogens and hydroxyls. Likewise it seems not improbable that a similarly constituted film plays a not inconsiderable part in surface tension phenomena at the interface of water and solids. Also the catalytic action of the surfaces of glass and other solids is well known. This also probably has its origin in this surface film and the glass probably acts as a catalyst by a mechanism similar to, if not identical with, that to be outlined in this paper in the case of aluminium oxide.

The great difficulty of removing all water from aluminium oxide and other compounds not having an available oxygen content is not found in the case of partially reduced oxides, whose interior oxygen is not wholly inaccessible. In the latter case the dissociated water layer is partially removed on raising the temperature quite moderately (450° in the case of partially reduced nickel oxide) whereas heating for hours in a blast lamp still leaves a water film on aluminium oxide particles. Presumably as the temperature of aluminium oxide is raised, more and more of the external layers of charged hydrogens and hydroxyls lose their charges and pass off as water. Whether the inner layers are, at the outset, held with the same tenacity as the outer ones, the former being more firmly held as the latter are removed, or whether there is, at the outset, a progressively diminishing tension in the layers from the inside to the outside, the fact is that as the water is gradually removed, it becomes increasingly difficult to remove the water remaining. There is still a water film on the surface, even after heating at atmospheric pressure at 500° C. for twenty hours, followed by two days heating with a Meker burner. In the case of reducible oxides the loss of surface film by heating at a much lower temperature results simultaneously in the loss of catalytic properties, as would be expected, since this film is the seat of the catalytic activity. The more complete loss of surface film in the case of a partially reduced oxide is directly connected with the fact that in this case the interior oxygen gradually comes into play, liberating all the hydrogen on the catalyst as free water, thus destroying at once both the surface film and the catalytic activity characteristic of partially reduced oxides.

It is true that this completely reduced oxide may still function as a catalyst by means of hydrogen contained in the pure metal. However, such a catalyst is much less effective, as has been pointed out in the paper dealing with catalysis by nickel. In such a catalyst the hydrogen appears to exist in two forms—(1) dissolved hydrogen which can be pumped out under vacuum and (2) positively charged hydrogens alternating with negatively charged hydrogens. This belief in the existence of hydrogen in this latter condition in metals has also recently been expressed by Bennewytz and Gunther.[2]

Another marked difference between the two types of catalyst arising from this same cause is found in the fact that a partially reduced oxide has a reduced metal layer overlying the unreduced oxide layer, and this reduced oxide layer probably carries the charged hydrogens and hydroxyls, whereas in the case of aluminium oxide the catalytic film of dissociated water lies wholly on the outer surface of each particle. This, in all probability, gives rise to the marked difference in behaviour of the two catalysts.

Thus, aluminium oxide is commonly known as a dehydration catalyst, while the members of the other group of partially reduced oxides are known as hydrogenation or dehydrogenation catalysts. In the latter case, as has been pointed out, the interior content of oxygen is vital to the restoration of the surface film, when it has been partially removed during the catalysis of hydrogenation of ethylene,[3] or the union of hydrogen and oxygen.[4] Indeed the movement of oxygen from the interior to the surface film appears, from the experiments recorded by Boswell and Bayley,[5] to take place so easily as to suggest that this movement may be vital to the whole mechanism of the catalysis of hydrogenation and oxidation. The absence of any available interior oxygen in aluminium oxide thus pushes into the background the catalysis of hydrogenation and oxidation, and determines that, when aluminium oxide is heated in contact with say ethyl alcohol at gradually rising temperature, nothing happens until both the hydrogens and hydroxyls of the surface film act simultaneously, drawing hydroxyl and hydrogen respectively from the ethyl alcohol and thus forming ethylene and water.

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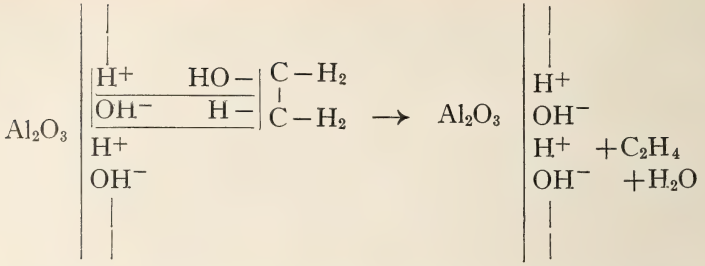
[2]Z. Physik Chem. 111, 275 (1924).

[3]Boswell, Trans. Roy. Soc. Canada, *16* III, 1 (1922).

[4]Boswell and McLaughlin, Trans. Roy. Soc. Canada, *17* III, 1 (1923).

[5]To be published.



The great tendency for the stable film to exist on the aluminium oxide leads to the immediate re-formation of the original catalytic complex and so the cycle can continue. However, although the dehydration catalysis of aluminium oxide predominates over the catalysis of hydrogenation and dehydrogenation, yet these latter are, as is well known,

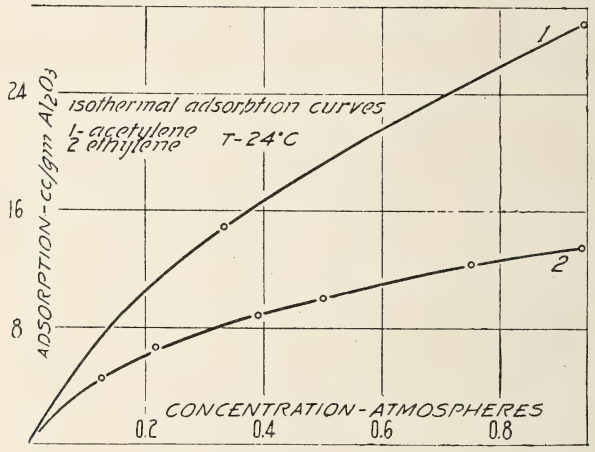
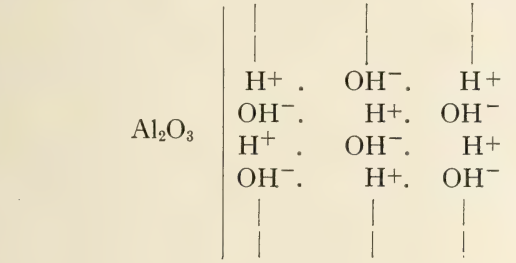


FIG. 1

not entirely suppressed. That is, the charged hydrogens and hydroxyls on the particles can under suitable conditions act independently as well as simultaneously. This matter will be discussed later in this paper.

Thus, aluminium oxide is known as a catalyst chiefly for reactions involving the removal of both hydrogen and hydroxyl from a compound, the so-called dehydration reactions. The theory indicates that it should also catalyse the addition of both hydrogen and hydroxyl to unsaturated compounds. The experimental data shows that both the transformation of ethylene and steam into ethyl alcohol, and of acetylene and steam into acetaldehyde, are catalysed by aluminium oxide. Likewise a catalyst of this constitution should catalyse the union of hydrogen and oxygen gases. This was found to be the case, the reaction setting in at 200° C. and proceeding rapidly at 250° C.

All the above reactions catalysed by aluminium oxide involve the elements of water, and in the two former either the addition or removal of water to or from the other reacting compound. Associated with this is the fact that aluminium oxide catalyst contains water, and the further fact that when this water content is diminished by heating at a high temperature the catalytic activity is likewise diminished. This all points to the conclusion that this catalyst functions by means of a surface film of water and that this film is the real seat of the catalysis. The marked stability of the film indicates that it is present in a special condition such as positively charged hydrogens and negatively charged hydroxyls, alternating with each other and completely enveloping each aluminium oxide particle. (See also paper on Platinum and Nickel.) This may be pictured thus:



As this is heated at gradually increasing temperatures the outer layers of dissociated water are removed as free water. The layers remaining are held with increasing tenacity, so that even at the temperature of the blast flame there is still some water left; at least one layer of charged hydrogens and hydroxyls remains. The catalyst has its maximum activity when used at a temperature of 350-400° C.

The chief catalytic use of aluminium oxide is for the transformation of alcohols into unsaturated hydrocarbons. A quantitative study was made of the gas changes involved in this reaction in the case of ethyl alcohol. The results recorded in the experimental part of this paper show that besides the formation of ethylene and ether by the removal of one mol of water from one and two mols of alcohol, considerable quantities of carbon, ethane and hydrogen are also produced. The formation of these latter has also been observed by other investigators. However, the quantitative results recorded here offer a simple explanation of the mechanism of what has occurred on the surface of the catalyst. For instance, it was found that 27 c.c. hydrogen and 18 c.c. ethane were formed, while the total carbon remaining on the catalyst gave on combustion 61 c.c. carbon dioxide and using up 71 c.c. oxygen in the process. Several theories can be devised which will satisfy different portions of

these measurements. But only two of these will fit the entire set of facts. One of these is: 36 c.c. ethylene was simultaneously hydrogenated to 18 c.c. ethane and dehydrogenated to 18 c.c. acetylene, $2C_2H_4 \rightarrow C_2H_6 + C_2H_2$. The ethane was liberated, giving the 18 c.c. ethane collected, while the 18 c.c. acetylene was polymerized and adsorbed on the catalyst. An independent experiment with acetylene showed that this in reality occurs. Then a reaction independent of this hydrogenation-dehydrogenation reaction occurred, whereby 13.5 c.c. ethylene was transformed into 27 c.c. hydrogen and free carbon. This hydrogen was liberated and collected while the carbon was adsorbed on the catalyst. The combustion of this adsorbed carbon to carbon dioxide would require 27 c.c. oxygen and give 27 c.c. CO_2. The combustion of the polymerized and adsorbed 18 c.c. acetylene to carbon dioxide and water would require 45 c.c. oxygen and give 36 c.c. CO_2. Thus, based on this explanation of what has transpired a total of 72 c.c. oxygen would disappear and 63 c.c. carbon dioxide would be produced. Actually 71 c.c. oxygen did disappear and 61 c.c. carbon dioxide were obtained. The second explanation differs from this latter only with respect to the hydrogenation-dehydrogenation reaction. This may consist in the hydrogenation of ethylene to ethane and the dehydrogenation of alcohol to acetaldehyde, thus $C_2H_5OH + C_2H_4 \rightarrow CH_3CHO + C_2H_6$ instead of the formation of one mol of ethane and one mol of acetylene from two mols of ethylene, as represented in the first interpretation. If this acetaldehyde is also completely adsorbed on the catalyst and subsequently burned to carbon dioxide, when oxygen is passed over the catalyst at a high temperature, the same amount of oxygen would be used up and the same amount of carbon dioxide would be formed as in the former interpretation. Probably both of these hydrogenation-dehydrogenation actions occur. In the experiment cited above, these secondary reactions had taken place to such a small extent (only 18 c.c. ethane were formed) that the acetylene or acetaldehyde had been completely adsorbed in a polymerized condition by the catalyst. The formation of free acetaldehyde observed when large quantities of alcohol have been transformed into ethylene, is probably due to the saturation of the catalyst with this acetaldehyde or a polymerization or condensation product of it, so that any further amount formed passes out of the reaction vessel as free acetaldehyde. The experimental data also shows that aluminium oxide catalyses the union of acetylene and water to form acetaldehyde. Similarly the union of ethylene and water to form ethyl alcohol is catalysed. Hence the following scheme shows the possible reactions, all of which are in harmony with the above qualitative and quantitative statements:

$$C_2H_4+C_2H_5OH \rightarrow C_2H_6+CH_3CHO$$

(1)

$$C_2H_4+C_2H_4 \rightarrow C_2H_6+C_2H_2$$
$$+H_2O \qquad +H_2O$$

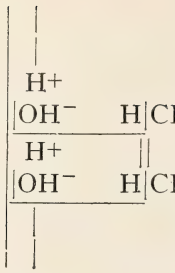
(2) $$C_2H_4 \rightarrow 2C+2H_2$$

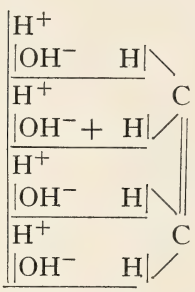
The inference seems justified that when ethyl alcohol vapour is passed over aluminium oxide at 350° C., besides the formation of ethylene and ether commonly observed, there is also the formation of ethane, acetaldehyde, acetylene, carbon, and hydrogen, the three former being produced by simultaneous hydrogenation and dehydrogenation and the two latter by the dissociation of ethylene, these two sets of reactions being quite independent.

One conclusion of this experiment is that aluminium oxide will not catalyse the union of ethylene and free hydrogen. However, this failure to catalyse the union of ethylene and hydrogen furnishes no argument against the existence of charged hydrogens and hydroxyls in the surface film, for, as we have found, the ethylene is itself altered and adsorbed in this altered condition on the aluminium oxide before the temperature necessary to effect its hydrogenation has been attained. The above quantitative relationships could not hold had any of the ethane had its origin in this reaction. Separate experiments show that ethylene and hydrogen are not catalysed to form ethane. Also since, as pointed out above, aluminium oxide can catalyse the transfer of hydrogen from ethyl alcohol to ethylene it is probable that in the presence of free oxygen, alcohol would pass directly to acetaldehyde, the oxygen acting as hydrogen acceptor in place of ethylene. The experiments performed by Duffill in this laboratory showed that considerable acetaldehyde could be obtained by passing alcohol vapour mixed with air over aluminium oxide at 350° C. in those cases where the apparatus was not destroyed by explosion.

The mechanisms of the various reactions catalysed by aluminium oxide receive a satisfactory interpretation if the catalyst has the constitution advanced in this paper. Thus

(1) Al_2O_3 with H^+, OH^-, H^+, OH^- and $HO|CH_2$, $H|CH_2$ $\rightarrow Al_2O_3$ with H^+, OH^-, $H^+ + C_2H_4 + H_2O$, OH^-

(2) Al_2O_3  $\rightarrow Al_2O_3+2H_2O+C_2H_2+C_2H_6$

(3) Al_2O_3  $\rightarrow Al_2O_3+4H_2O+2C+2H_2$

That is, the initiation of the reactions comes from the charged hydrogens and hydroxyls on the aluminium oxide particles. These react with the hydrogens or hydroxyls, or both, in the compounds brought in contact with the heated surfaces, thus setting up the reactions which always result in the formation of as much water as has been removed from the catalytic surface. The surface film is restored and the cycle continues. Or it may be that the charged hydrogens and hydroxyls are not actually removed from the surface, in all reactions, but remain in place, while exerting attractions upon the oppositely charged hydroxyls and hydrogens in the compounds brought in contact with the surfaces, thereby weakening the attractive forces holding the constituent atoms of these compounds together and thus enabling a readjustment to a more stable condition of equilibrium to be rapidly attained.

From this point of view the initial system (say ethyl alcohol), while having a smaller entropy than the final system into which it is transformed by the catalyst (an equilibrium mixture of ethyl alcohol, ethylene and water), yet cannot alone effect any measurable change at the temperature at which the catalyst can rapidly bring it about (350° C. in this case), owing to the stability of the molecules of the bodies comprising the original system (ethyl alcohol in this case). The catalyst interjects the loosening effect referred to above by means of attractions due to the dissociated water constituting the surface film, and thus enables the system to pass rapidly towards the final equilibrium condition of maximum entropy.

The catalyst from this point of view does not accelerate a reaction

already in progress notwithstanding that the final system has a greater entropy than the original system, but actually initiates the change from the one to the other. This does not imply any violation of the second law of thermodynamics, for the transformation from the initial to the final system is not completely reversible. The system cannot return to pure alcohol.

Adsorption on Al_2O_3.

Perhaps the most convincing support for the theory presented in this paper comes from the facts of adsorption of gases and electrolytes on aluminium oxide. It seemed to us highly probable that the phenomena associated with adsorption, not only of gases, but also of electrolytes from water solutions, are influenced more by these surface water films than by any other factor. The commonly accepted view in the case of water solutions of electrolytes pictures the adsorption of the salt BA as follows:

$$BA + H.OH \longrightarrow B.OH + HA.$$

where the salt BA is hydrolysed in a reversible reaction to a slight extent, followed by adsorption of either the base B.OH or the acid HA on the adsorbing material. If the specific adsorption is of the base B.OH, then the presence of hydrogen-ion in the solution, moving the above equilibrium to the left, diminishes the amount of adsorption, while the addition of hydroxyl ion produces the reverse effect, and increases the adsorption. Likewise, if the specific adsorption is for the acid HA, then the effect of the addition of hydrogen ion or hydroxyl ion to the solution of BA is just the reverse. But this says nothing about the mechanism of the actual adsorption of the acid or base on the adsorbing material. The full interpretation of the whole mechanism must, of course, involve a knowledge of (1) the relationship of the electrolyte to the solvent water, and (2) the nature of the adsorption surface. The senior author suggests the hypothesis presented here of the nature of the surface film of aluminium oxide particles, as the second part of this mechanism. Without modifying at all the usually accepted view that the salt BA exists in solution as B^+ ions and A^- ions and undissociated mols BA, could not the mechanism of adsorption of the cation B^+ and the accumulation of H^+ ion in solution be with equal force represented by the scheme:

$$\begin{array}{|l} \\ \\ H^+ \\ OH^- + BA \\ H^+ \\ OH^- + BA \\ \\ \\ \end{array} \quad Al_2O_3 \quad \longrightarrow \quad \begin{array}{|l} \\ \\ B^+ \\ OH^- \\ B^+ \\ OH^- \\ \\ \\ \end{array} \quad Al_2O_3 \quad + 2H^+ + 2A^-$$

However, the particular states of B and A and BA and their relationships to the water intervene, and must play a vital part in the adsorption. The senior author hopes to present experimental evidence in connection with this problem of electrolytes in solution in the near future, which may help in the solution of the first part of the mechanism, mentioned above, of adsorption from solution.

Turning to the adsorption of ethylene on aluminium oxide, it seemed that if this also is dependent on the surface water film, its amount should increase as the extraneous free water covering the active film is removed, but should then gradually decrease as this active film diminishes, until, when the water is entirely gone, no adsorption whatever would occur.

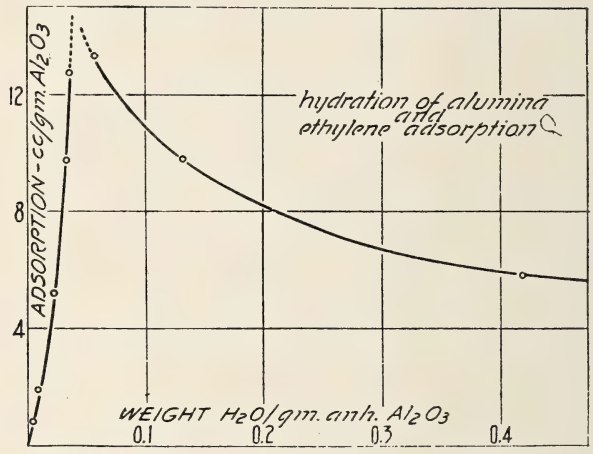


FIG. 2

The following measurements show that this is precisely what happens. The curve (Fig. 2) makes this quite clear. The maximum adsorption occurs with the water content of about 4%. As the water content either increases or diminishes from this amount the adsorption diminishes. Below this water content of 4% the amount of the adsorption falls off extremely rapidly. After the final heating in the Meker burner for two days the adsorption has fallen almost to zero. The conclusion is unavoidable that the union of ethylene with aluminium oxide is directly connected with this water film. Now it is a well-known fact that the catalytic properties of aluminium oxide very markedly diminish on prolonged heating of the oxide at high temperatures. This is, no doubt, due to the partial loss of this active water film. That heating does not completely inhibit this activity is due to the fact, which will be shown presently, that even after heating at 500° C. for twenty hours, followed

by heating in a Meker burner for two days, there is still a very small amount of water on the particles. These facts regarding adsorption of ethylene and catalytic activity of aluminium oxide show, not that the catalytic decomposition of ethyl alcohol to ethylene is due to the marked capacity of aluminium oxide to adsorb ethylene, but that both the catalytic properties and the capacity for adsorption are due to the water film on the particles. The remarkable stability of the film indicates that it exists in a very special condition, which, we believe, is due to the existence of oppositely charged hydrogens and hydroxyls in a state of great tension surrounding the particles of aluminium oxide. When it is found, as already pointed out in this paper, that aluminium oxide, especially when heated to 350° C., so as to leave the water content around 4%, is an active catalyst for reactions involving the addition, simultaneously, of hydrogen and hydroxyl to compounds, and the splitting off of hydrogen and hydroxl from compounds simultaneously, belief in the validity of the hypothesis is, we believe, very considerably increased.

In view of the great stability of this surface film it is not surprising that it should exert a great protection for an underlying interior content of oxygen. This oxygen is not available in the case of aluminium oxide. But in the case of partially reduced nickel oxide, iron oxide, platinum black, etc., such oxygen does exist, and the protective power of the surface film has been shown in this laboratory. The senior author hopes to publish shortly experimental data showing similar behaviour by dissociated films of analogous constitution formed by the partial reduction of chlorides, sulphides and nitrides.

EXPERIMENTAL

Materials

The aluminium oxide used in all the experiments was prepared in the following manner: 400 grams metallic aluminium were dissolved in a solution of 2,000 grams sodium hydroxide in 3 litres water. The solution was diluted to 6 litres, heated to boiling and allowed to stand. A precipitate settled out and the clear liquid above was siphoned off. A quantity of nitric acid was added, insufficient, however, to neutralize the sodium hydroxide, the whole heated to boiling, thus precipitating any iron as ferric hydroxide. This was filtered off. Nitric acid was now added in excess so as to redissolve the aluminium hydroxide precipitated at first. Ammonium hydroxide was added slowly with stirring to the hot solution to precipitate the aluminium as hydroxide. This was washed in tall cylinders by decantation for many days until the filtrate gave no reaction for ammonia, filtered on a perforated funnel and dried

in an air oven at 110° C. The resulting material was ground up in a mortar to a coarse powder.

The ethylene used was made by the phosphoric acid method of Newth, care being taken to remove ether by condensation and to avoid the collection of air along with the ethylene. Traces of oxygen in the gas used in the experiments were removed by shaking with alkaline pyrogallol.

The acetylene used was made from commercial calcium carbide.

The nitrogen and oxygen used were from cylinders of the compressed gases. Traces of oxygen were removed from the nitrogen by passage over heated copper.

The hydrogen was electrolytic hydrogen.

The action of the catalyst with hydrogen-oxygen mixtures.

Dry mixtures of hydrogen, oxygen and nitrogen were passed over the aluminium oxide which had previously been heated for twelve hours to 360° C. in an atmosphere of nitrogen. The apparatus was similar to that used in studying the reduction of nickel oxide. The train consisted of two calibrated water-jacketed burettes of about 400 c.c. capacity between which was placed a pyrex glass tube three-quarter inches in diameter and twenty inches long containing about 25 grams of the aluminium oxide which could be heated in an electric furnace to various desired temperatures which latter were measured by a standard thermometer inserted alongside the reaction tube in the furnace. Between the reaction tube and each burette were placed two U-tubes containing, in the hydrogen-oxygen experiments, concentrated sulphuric acid on pumice, and in the ethylene and acetylene experiments, fused calcium chloride.

The temperature was gradually raised from room temperature to 365° C. and the temperature at which the expansion, due to the rise in temperature, was noticeably retarded by the contraction, due to the combination of hydrogen and oxygen, was noted. After the completion of the reduction the total contraction was measured at room temperature and the gas was analysed. It was found that with a gas mixture of the composition 21.0% hydrogen, 30.7% oxygen and 48.3% nitrogen, the reaction set in at 210° C., was proceeding rapidly at 250° C. and soon ran to completion at 365° C. Gas analysis showed that no hydrogen remained; the contraction in volume was approximately that calculated for a combination of all the hydrogen originally present. Also with a gas mixture of the composition 43.0% hydrogen, 15.8% oxygen, 41.2% nitrogen, the reaction set in at about 200° C. When no further contraction was observed at 365° C. the gases showed on analysis that no oxygen remained. The contraction, on cooling to the original tempera-

ture, was approximately that calculated for a combination of all the oxygen originally present.

Thus the combination of hydrogen and oxygen is catalysed by aluminium oxide, the reaction setting in at about 200° C. and proceeding with rapidly increasing velocity as the temperature is raised.

The action of the catalyst on ethyl alcohol

It is well known that in the manufacture of ethylene from ethyl alcohol using aluminium oxide heated to 350° C. as catalyst, the latter becomes dark coloured, indicating a deposition of carbon or a tarry material, or both. Also the formation of acetaldehyde and ether in this reaction is well known.

It would seem probable that the carbon, if present, could form by the simultaneous hydrogenation and dehydrogenation of ethylene thus (1) $3C_2H_4 \rightarrow 2C_2H_6 + 2C$ or the dissociation of ethylene thus: (2) $C_2H_4 \rightarrow 2C + 2H_2$ or (3) the simultaneous hydrogenation and dehydrogenation of ethylene to ethane and acetylene and the dissociation of the acetylene so produced, thus: $C_2H_2 \rightarrow 2C + H_2$. The tarry constituent of the deposit might form by the polymerization of acetylene or acetaldehyde. It thus seemed desirable to carry out an experiment as nearly quantitatively as possible, with a view to determining (1) the volume of hydrogen formed, (2) the volume of ethane formed, (3) the volume of oxygen consumed in burning the deposit completely to carbon dioxide and water, and (4) the volume of carbon dioxide produced in this latter operation. It seemed also very desirable in this experiment to observe a further condition, viz., to run the experiment for only a short time, so that should the tarry part of the deposit be due to the polymerization of acetylene or acetaldehyde, none of the acetylene or acetaldehyde should escape from the tube, but should be all caught by the long layer of aluminium oxide in the polymerized form.

Apparatus used

About 75 c.c. ethyl alcohol was slowly distilled in an atmosphere of nitrogen over the catalyst at 360° C. The issuing gases were passed first through a long water-jacketed condenser into a receiver which in turn was connected with two efficient washers containing 40% bromine in strong solution of potassium bromide in water, followed by two washers containing potassium hydroxide solution (1:1), then through a spiral glass condensing tube immersed in alcohol-carbon dioxide snow contained in a Dewar flask, and from this into a gas holder from which portions were taken for analysis.

Analysis of the gas collected showed the presence of hydrogen 27 c.c. and ethane 18 c.c. at 25° C. and 758 mm. pressure.

A measured volume of oxygen was then passed between the burettes across the heated aluminium oxide. The weight of carbon dioxide formed and the volume of oxygen used were measured with due regard to temperature and pressure. It was found that 71 c.c. oxygen calculated to 25° C. and 758 mm. pressure were used up and 61 c.c. carbon dioxide calculated to the same temperature and pressure were formed.

The Hydrogenation of Ethylene

The experiment just described indicated that the combination of ethylene and hydrogen is not catalysed by aluminium oxide. It seemed desirable to verify this by an experiment set up for the purpose. Accordingly carefully purified hydrogen, mixed with ethylene (99.4%) in known proportions, was passed between burettes over aluminium oxide starting at 250° C. and rising in steps to 340° C. The combination, if it occurred, of course, would have been indicated by a decrease in volume. Owing to the adsorption of ethylene on aluminium oxide care was necessary in order not to confuse these two possible causes of any diminution in volume. However, although this adsorption is, as will be shown presently, very considerable at 25° C. and 1 atmosphere pressure (about 11 c.c. per gram) it is comparatively small at 253° C. (about 1 c.c. per gram). At a partial pressure of one half an atmosphere, which was approximately that used in the experiments, the amount of adsorption is, of course, much smaller (about 5/7 for 25°, of the adsorption at one atmosphere). Hence, using 20 grams aluminium oxide at 253° C. an adsorption of about 12 c.c. of ethylene, at 319° C. of about 6 c.c., and at 385° C. of about 4 c.c., was to be expected. On passing a mixture of 155 c.c. ethylene and 162 c.c. hydrogen over about 20 grams Al_2O_3 at 253° C. there was in five minutes a diminution in volume of 10 c.c., which did not alter on passing the gas mixture back and forth for a further 65 minutes. This diminution was due undoubtedly to adsorption, and, if hydrogenation was taking place at all, the rate was negligibly small. Also the aluminium oxide showed none of the discoloration which always occurs, and is easily observable, when ethylene undergoes dissociation in the presence of aluminium oxide. The apparatus was swept out with nitrogen and a mixture of 180 c.c. ethylene and 163 c.c. hydrogen passed at 319° C. There was a loss in volume of 2 c.c. in the first 5 minutes, and no further change in 65 minutes. There was no discoloration of the aluminium oxide. The temperature was now slowly raised to about 380° C., occupying almost 100 minutes. At 380° C. the discoloration of the aluminium oxide and the slow increase in volume showed that ethylene was dissociated. On raising the temperature to 500° C. the volume and discoloration greatly increased. Hence, the first indication of any reaction was discoloration accompanied by

increase in volume. Ethylene alone was passed over another sample of aluminium oxide when the same behaviour was found in all particulars, as in the case of the ethylene-hydrogen mixtures. It would seem, then, that if hydrogenation of ethylene to ethane does occur it is a very slow reaction, and is insignificant compared with the reaction involving the dissociation of ethylene. Hence, the conclusion arrived at from the quantitative study of the action of ethyl alcohol and aluminium oxide, that the formation of ethane observed in the alcohol-aluminium oxide reaction does not arise from union of free hydrogen and ethylene, appears to be confirmed.

The action of acetylene and aluminium oxide

The quantitative experiment of the action of ethyl alcohol and aluminium oxide already described indicates that acetylene is formed by the reaction $2C_2H_4 \rightarrow C_2H_2 + C_2H_6$. It seemed desirable to determine the action of acetylene alone on aluminium oxide in order to determine to what extent polymerization takes place and at what temperature it sets in. For the interpretation given of the measurements implies a very rapid polymerization of acetylene at 350° C. and adsorption on the aluminium oxide. About 15 grams aluminium oxide was saturated with acetylene at room temperature. 438 c.c. was adsorbed. The tube containing the aluminium oxide was connected at each end with a burette and slowly heated in an electric furnace, the volume being noted. At 100° C. the volume in the burette had increased by 278 c.c., at 110° C. by 291 c.c., at 120° C. by 296 c.c. As the temperature rose above 120° C. the volume slowly diminished. At 135° C. the diminution was much more rapid, the volume in a few hours falling to 78 c.c. 300 c.c. additional acetylene was added, making the volume 378 c.c. In a few hours this had fallen to 246 c.c. The aluminium oxide was now deep brown in colour, and on extraction with benzene and evaporating the solvent a few drops of an aromatic oil were obtained. Thus, acetylene, even below 150° C., is rapidly polymerized and absorbed by aluminium oxide. The conclusion before drawn, that at 350° C. the relatively small amount of acetylene slowly formed in the experiment (18 c.c. in all, along with 18 c.c. of ethane) was polymerized and completely adsorbed on the aluminium oxide, seems to be justified.

The Reaction of Ethylene and Steam

Ethyl alcohol has been made by Wibaut and Dieckmann[6] by passing ethylene and steam over aluminium oxide at 300-400° C. This was repeated at a temperature of 300-350° and alcohol was detected in the

[6]Chem. Abs. *17*, 3858 (1923).

reaction product by transformation into, and isolation of, iodoform. The yield is poor under these conditions. However, there is no doubt that aluminium oxide is a catalyst for the reaction $C_2H_4+H_2O \rightarrow C_2H_5OH$.

The Reaction of Acetylene and Water

Acetylene and steam were passed over aluminium oxide at 160°-170° C. The reaction products were passed through a water condenser and then through a flask immersed in a freezing mixture. The distillate gave a precipitate of silver with ammoniacal silver nitrate solution and also a precipitate with Fehling's solution. The experiment was repeated at 240°-250° C., 3.5 liters acetylene being passed along with steam. The reaction product was distilled. The fraction boiling below 100° C. was collected separately and was found to give a silver mirror and a copious precipitate of silver with ammoniacal silver nitrate, also a copious red precipitate with Fehling's solution. A considerable amount of higher boiling liquid was obtained up to 120° C., leaving a residue which, although giving no reaction with ammoniacal silver nitrate at first, did so on prolonged boiling indicating the probable existence of paraldehyde. Thus aluminium oxide catalyses the union of acetylene and steam to form acetaldehyde.

The Reaction of Aluminium Oxide and Acetaldehyde

The above experiments showed that acetylene is polymerized and adsorbed in this polymerized condition by aluminium oxide at temperatures above 135° C. It seemed desirable to determine whether the dehydration of acetaldehyde to acetylene would occur at all at temperatures around 135°. Accordingly the vapour of acetaldehyde was passed over aluminium oxide at about 135° C. No acetylene or other gas was observed. However, the catalyst turned a deep brown and an oily liquid was obtained by distilling the reaction product. The experiment was repeated at 300° C. with the same result. The aluminium oxide after the reaction gave an oil on distillation. In view of the behaviour of acetylene alone with aluminium oxide it is probable that if acetylene had been formed in passing acetaldehyde, it had been polymerized and adsorbed. Also the condensation of acetaldehyde to form crotonic aldehyde and other condensation products might easily happen.

Thus, aluminium oxide can catalyse the following reactions involving simultaneously, hydrogen and hydroxyl:

(1) The dehydration of ethyl alcohol to ethylene.

(2) The combination of ethylene and water to form ethyl alcohol.

(3) The combination of acetylene and water to form acetaldehyde.

Also the following reactions accompanying the formation of ethylene from ethyl alcohol are catalysed by aluminium oxide:

(1) The simultaneous dehydrogenation of ethylene to acetylene (which is adsorbed in a polymerized condition on the aluminium oxide) and the hydrogenation of ethylene to ethane.

(2) The dissociation of ethylene to carbon and hydrogen. It has been shown that the combination of free hydrogen and ethylene to form ethane is not catalysed by aluminium oxide, as the dissociation is a very much faster reaction.

The Adsorption of Ethylene and Acetylene on Aluminium Oxide

On passing these gases separately over aluminium oxide in the course of the experiments just described, the very large power of adsorption of aluminium oxide for these gases, particularly at room temperature, was noticed. It was decided to measure the amount of this adsorption, and, to some extent, its variation with temperature and pressure.

The aluminium oxide used in these determinations was made according to the method described at the beginning of the experimental part of this paper. It was dried in an ordinary air bath at 110° C. for 8 hours and in a glass tube at 360° in a current of nitrogen for 6 hours. 18 grams of this material was used. This was placed in a pyrex tube, which was connected at each end with a U-tube containing calcium chloride, and these U-tubes were each connected to a 400 c.c. water jacketed and calibrated gas burette. Various partial pressures of ethylene and nitrogen were used, the composition at equilibrium being determined in each case by gas analysis, using bromine in the gas absorption pipette. Another series of measurements, using acetylene, was also made, using the same procedure. The following table and graph show the results of these measurements.

Ethylene Adsorption at 24° C.

Partial Pressure (At.)	Ethylene, Adsorbed c.c.	c.c. per gram of Aluminium oxide used
0.940	242	13.4
0.750	224	12.3
0.502	180	10.0
0.390	160	8.9
0.214	120	6.7
0.124	83	4.6

Acetylene Adsorption at 25° C.

Partial Pressure (At.)	Acetylene Adsorbed c.c.	c.c. per gram of Aluminium oxide used
0.946	517	28.7
0.331	267	14.8

It is seen that in the case of ethylene the adsorption curve follows the general form of those for carbon monoxide on charcoal and platinum. Also the absolute values are almost as great. Although not sufficient points on the acetylene curve have been determined to definitely fix the whole curve, yet it is seen that the adsorption of acetylene on aluminium oxide at pressures above about 9/10 of an atmosphere is more than double that of ethylene, and amounts at a pressure of .946 atmospheres to 28.7 c.c. of acetylene per gram of the aluminium oxide used. This is comparable with the adsorption of carbon monoxide on cocoanut charcoal, which has always been considered very large.

Variation of ethylene adsorption with temperature

The same apparatus was used as in the latter measurements. The tube was heated in an electric tube furnace and every trace of oxygen was removed from the ethylene by shaking with alkaline pyrogallol. The tube containing the aluminium oxide of the first ethylene adsorptions already recorded was heated in a current of nitrogen to a temperature of 360° for 5 hours. The following are the results obtained:

Temp. °C.	Adsorption of ethylene c.c. adsorbed (.580 atmospheres)	c.c. adsorbed per g. of oxide used
24	196	10.9
242	21	1.2
378	13	0.7

The adsorption value for 378° C. must necessarily be only approximate, because, as already pointed out, at 350° C. and higher ethylene undergoes various reactions which could interfere with the accuracy of an adsorption determination. However, as the former reactions occur relatively slowly, while the reading at 378° occupied relatively a short time, it is probably very close to the correct value.

The variation of the adsorption of ethylene with variation in the amount of water in the aluminium oxide

From the standpoint of the theory presented in this paper the determination of the nature of this variation is of the greatest importance.

A quantity of aluminium oxide, prepared as already described, was placed in a pyrex tube and steam passed over for one hour at 110° C. The sample now weighed 25.7350 g. Nitrogen was passed to expel air and the tube containing the oxide was placed in a train consisting of a water-jacketed and calibrated burette, a U-tube containing calcium chloride, the tube containing the oxide, another U-tube containing calcium chloride and a second burette similar to the first one. The apparatus between the burettes being filled with nitrogen, a measured

volume of ethylene was passed back and forth until equilibrium was attained, and the volume of ethylene adsorbed was measured. The gas in the burette was discarded and another 350 c.c. ethylene was introduced into the burette and the adsorption again measured. This was continued until no further adsorption was obtained on adding fresh ethylene. The sum of the various adsorptions gave the total volume of ethylene, adsorbed by the aluminium oxide at 24° C., containing an amount of water which later was calculated. This same sample of oxide containing adsorbed ethylene was now heated at a given temperature in a current of nitrogen, the water given off being weighed. The adsorption

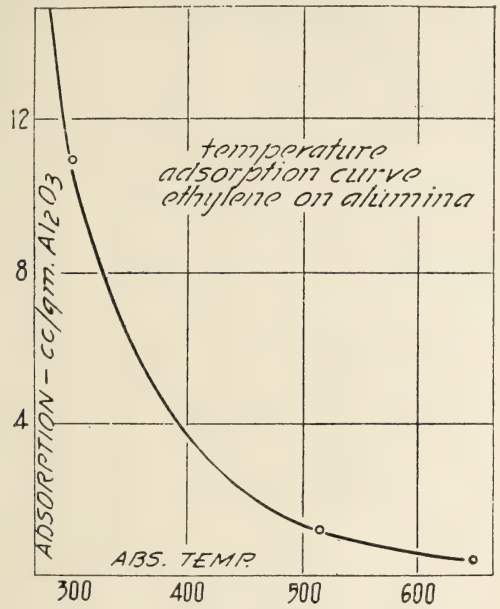


FIG. 3

of ethylene at 24° C. was again measured. A further heating in nitrogen at a still higher temperature was carried out, the water determined and another ethylene adsorption was measured. This procedure was continued until the adsorption of ethylene on aluminium oxide which had been heated at 500° for 70 hours had been measured. The aluminium oxide in this condition was transferred quantitatively to a weighed crucible and the heating continued with a Meker burner for various lengths of time, the water expelled by each heating being weighed and the ethylene adsorption at 24° C. after each heating being determined in the apparatus already described. Weight of aluminium oxide at the completion of the measurements was 18.3100 g. The measurements are recorded in the following table and plotted in curve 3.

Ethylene adsorbed c.c.	Temp. of heating °C.	Length of time of heating hours	Weight of aluminium oxide sample grams	Water off grams	c.c. ethylene per gram aluminium oxide as present at end of series	c.c. of ethylene per gram aluminium oxide anhydrous
106			25.7350		5.79	5.81
	300	—		5.0800		
179			20.6550		9.78	9.81
	400	20		1.3750		
242			19.2800		13.22	13.26
	500	20		0.3830		
232			18.8970		12.67	12.72
	500	50		0.0450		
176			18.8520		9.61	9.64
	Meker	4		0.2510		
96			18.6010		5.24	5.26
	Meker	12		0.2030		
35			18.3980		1.91	1.92
	Meker	96		0.0880		
15			18.3100		0.82	0.82
				0.0660		

By extrapolation from the last two adsorptions the water still on the oxide was 0.0660 g. This was calculated from the following equation where x is the water:

$$\frac{\frac{x}{18.31-x}}{\frac{x+.0880}{18.31-x}} = \frac{15}{35}$$

$$x = 0.0660$$

Hence the weight of anhydrous aluminium oxide used in these experiments was 18.2440 g. Thus, the water still present on the oxide after the various heatings was 0.36% of the total weight.

SUMMARY

A mechanism is suggested for the action of aluminium oxide as a catalyst.

A mechanism is suggested for the adsorption of electrolytes from water solutions on aluminium oxide.

The adsorption of ethylene and acetylene on aluminium oxide for several partial pressures has been measured.

The variation of adsorption of ethylene on aluminium oxide with variation of temperature has been determined.

The variation of adsorption of ethylene on aluminium oxide with variation of water content has been determined.

The action of ethyl alcohol and aluminium oxide at 350° C. has been quantitatively studied. Besides the formation of ethylene, commonly observed, the following reactions occur:

$$2\ C_2H_4 \longrightarrow C_2H_6 + C_2H_2 \qquad (1)$$

$$C_2H_4 \longrightarrow 2C + 2H_2 \qquad (2)$$

The acetylene in (1) is polymerized and adsorbed on the aluminium oxide along with the carbon from (2). Ethane is formed solely by reaction (1), none being formed by the addition of free hydrogen to ethylene.

It has been shown that aluminium oxide will catalyse the union of ethylene and water to form ethyl alcohol, also the union of acetylene and water to form acetaldehyde, also the union of hydrogen and oxygen.

The actions of aluminium oxide with ethylene and hydrogen mixtures, with ethylene alone, with acetaldehyde and with acetylene have been studied.

THE INFLUENCE OF POURING TEMPERATURE AND MOULD TEMPERATURE ON THE PROPERTIES OF A LEAD-BASE ANTI-FRICTION ALLOY

By O. W. Ellis, *Assistant Professor of Metallurgical Engineering*

I. Preliminary Investigation

In this investigation three alloys were used. They were prepared by melting together suitable proportions of lead, of tin, and of two stock alloys, previously prepared, of the following compositions:

Antimony-lead stock alloy.....17.7 per cent. Sb, 82.3 per cent. Pb
Copper-tin stock alloy.....30.0 " Cu, 70.0 " Sn

No attempt was made to analyse any of these alloys, but, since exceptional care was taken in their preparation, the test alloys must have approximated closely in analysis to the following values:

Alloy.	Lead. Per Cent.	Antimony. Per Cent.	Tin. Per Cent.	Copper. Per Cent.
A	85	10	5	nil
B	80	15	5	nil
C	80	15	3.5	1.5

While hardness tests were made on these alloys and photomicrographs were taken of typical sections, it is felt unnecessary to refer to them here, since the questions of structure and hardness were taken up more fully in the later investigations. The results of the compression tests, however, are felt to be of sufficient interest to merit attention, and they are, on this account, shown graphically in Figs. 1 to 3. A study of the curves presented in these diagrams will serve to demonstrate the general correctness of the following conclusions, based on the results of this preliminary study:

1. The replacement of lead by antimony increases the resistance of these alloys to compression. It may be added that the replacement of lead by antimony was also found to increase their hardness (Brinell) —*cf.* the results of the author's previous work.[1]

[1] *J. Inst. Metals*, 1918, 19, 151.

2. The replacement of tin by copper increases the resistance of these alloys to compression. The Brinell hardness, however, is scarcely affected by this substitution.

3. Mould temperatures exert a more powerful effect on the mechanical properties of these alloys than do pouring temperatures.

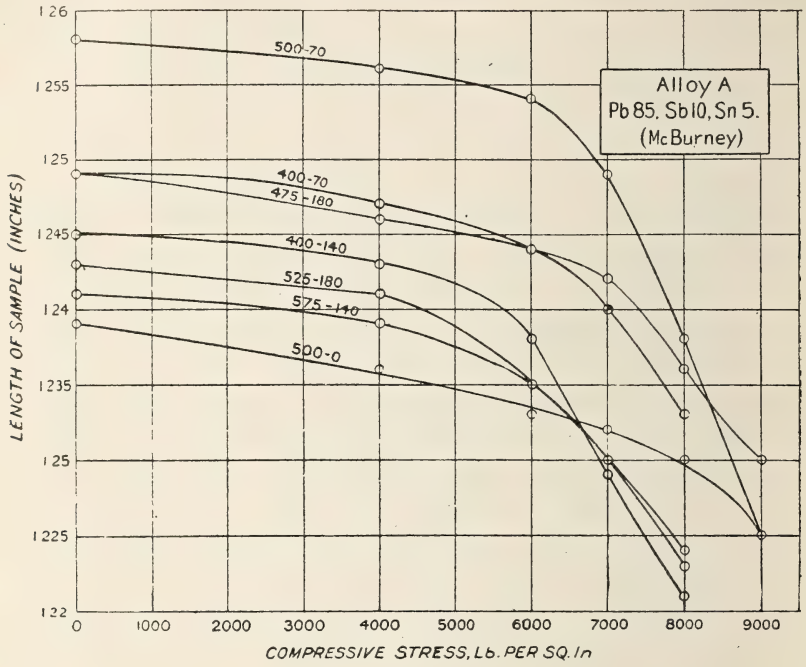


Fig. 1

II. Investigation of a Lead-Base Bearing Metal free from Copper

There was selected for examination an alloy of the following composition:

	Per Cent.
Lead	83.1 (by difference)
Antimony	12.1
Tin	4.8

This alloy was chosen in preference to others because it approached more closely in composition to the alloy which, other things being equal, was found by the author (*loc. cit.*) to be possessed of the best "all-round" mechanical properties.

Microscopic examination of this alloy shows it to consist of a matrix of antimony-lead eutectic, wherein are embedded cubes of the antimony-tin compound, SnSb. The structures both of the eutectic and the

compound are signally affected by variations in those factors which are associated with pouring.

From an ingot of the above alloy, supplied by the Canada Metal Company, of Toronto, considerably more than sufficient was removed to suffice for each experiment. This amount of alloy was introduced into a large ladle and slowly heated to the pouring point. Its temperature was continuously noted by means of a base-metal thermocouple, which was enclosed in a silica tube. The latter served as a rod with which the molten alloy was occasionally stirred.

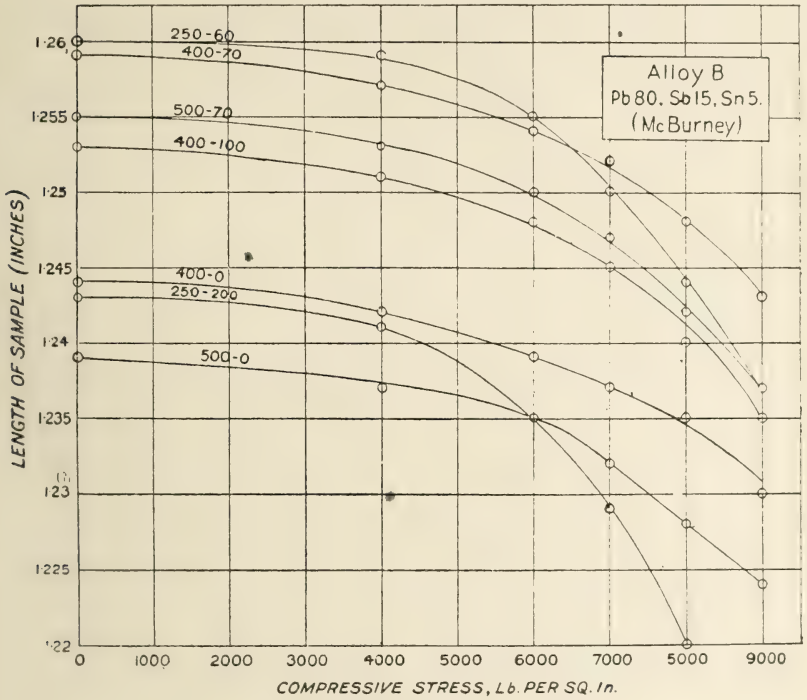


Fig. 2

From the ladle the melt was poured into duplicate steel moulds, which were of such dimensions that ingots 2 in. long, 1.5 in. in diameter at the top, and 1 in. in diameter at the bottom, were obtained (see Fig. 4).

Altogether five pouring temperatures and three mould temperatures were used. These are tabulated below:

Pouring Temperatures °C.					Mould Temperatures °C.
300	350	400	450	500	0
300	350	400	450	500	100
300	350	400	450	500	200

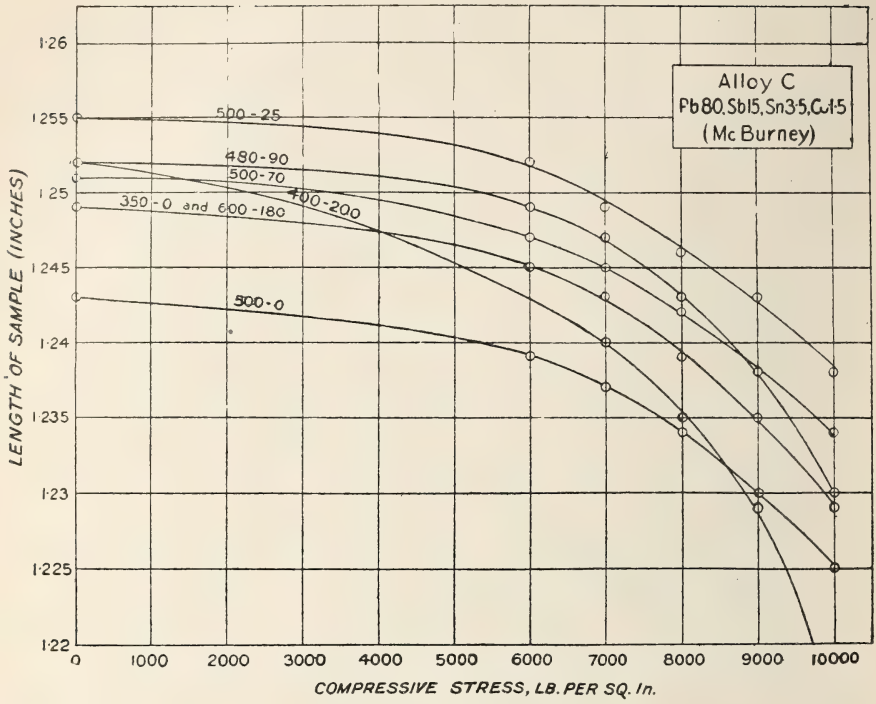


Fig. 3

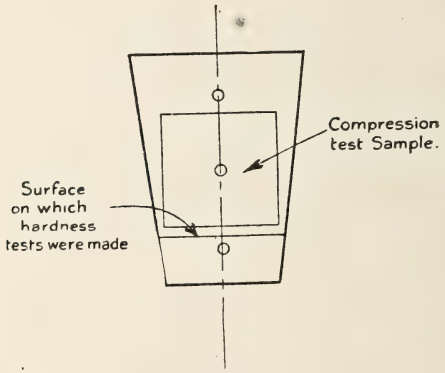


Fig. 4.—Drawing showing positions of compression and hardness test samples relative to ingot. Photomicrographs were made at areas approximating in position to those shown by the circles.

The following method of taking mould temperatures was adopted: into each of the moulds a closely fitting metal plug was introduced. In these plugs holes had been drilled. These holes were filled with mercury, into which thermometers were dipped. It was assumed that

the plugs approximated so closely to the moulds in temperature that they could be taken as representing quite satisfactorily the temperature of the moulds themselves. The moulds were cooled to 0° C. by standing them, subsequent to thorough drying, in a bath of iced water; to 100° C. by standing them in boiling water; and to 200° C. by standing them on an electric hot plate, covered by an inverted graphite crucible, through a hole in the bottom of which the thermometer employed in reading the temperature of the mould was inserted. Duplicate casts were made at each pouring temperature and mould temperature.

Determinations were also made of the times occupied in the cooling of castings poured under conditions similar to those under which the test castings were made. The method used in determining these times was as follows:

A standard mould, heated to the desired temperature, was rapidly filled with molten alloy. When completely filled a note of time was made. While the casting cooled a No. 20 S.W.G. Nichrome wire was moved up and down its vertical axis about twice per second. Observations of the condition of the casting could thus be quite satisfactorily made. When it was quite solid the time was again noted. The difference between the times noted, which gave the time taken by the casting to cool from the pouring temperature to the point of complete solidification, was recorded for each of the castings, at least two observations of this difference being made in each case. The results of these determinations are quoted in column 4 of Table I.

In the case of certain of the castings whose times of cooling were relatively long observations were made of both (1) the times taken by the castings to reach the liquidus, and (2) the times taken by the castings to cool from 255° C. (the liquidus) to 245° C. (the solidus)—that is, of course, to the point of complete solidification of the eutectic. The latter times—the freezing times—are quoted in column 5 of Table I.

In this table are also shown the calculated reciprocals of the cooling times of the alloys, which, it is thought, may be assumed to be proportional to some function of their rates of freezing. In this connection it is interesting to observe in what way the mean rates of freezing of the slowly cooled alloys agree with the reciprocals of their times of cooling—*cf.* columns 6 and 7 of Table I.

Before entering upon a discussion of the results of the hardness and compression tests made on the castings of this alloy, it will be well to consider photomicrographs representative of their structures. Three photomicrographs were taken of each of the castings. Sections representative of the structure at points near the top, the middle, and the bottom of each of the castings were examined in each instance.

Reference to the photomicrographs, Figs. 8-18 (Plates I and II),

TABLE I

1	2	3	4	5	6	7	8	9									10	
								Compression Test									Compression Test	
								Percentage Compression of Sample under Increasing Stress (lb. sq. in.)										
Number of Casting	Temperature of Mould. °C.	Temperature of Pouring. °C.	Total Cooling Time (secs.)	Freezing Time (secs.)	Reciprocal of Cooling Time	Mean Rate of Freezing (°C. per sec.)	Rockwell Hardness Number (Average)	1275	2550	3825	5100	6375	7650	8925	10,200	11,475	Stress at Rupture	Percentage Compression
1	0	300	21	..	0.048	..	91.5 (7)											
2	"	350	22	..	0.045	..	90.7 (6)	..	..	..	0.14	0.35	0.50	1.03	1.83	P.F.	19,100+	38.53
3	"	400	23	..	0.043	..	92.2 (8)	..	..	0.02	0.14	0.32	0.66	0.87	1.45	P.F.*	19,100+	33.16
4	"	450	26	..	0.038	..	91.2 (8)	..	..	..	0.17	0.34	0.87	0.96	1.32	P.F.	19,100+	34.86
5	"	500	32	..	0.031	..	91.8 (6)	..	..	0.07	0.14	0.22	0.47	0.82	1.15	P.F.	19,100−	37.61
6	100	300	36	..	0.028	..	90.0 (7)	..	..	0.06	0.11	0.28	0.55	1.14	P.F.	..	20,375+	36.03
7	"	350	38	..	0.026	..	88.4 (6)	..	0.02	0.09	0.19	0.41	0.72	1.23	P.F.	..	19,100+	32.55
8	"	400	42	..	0.024	..	88.8 (7)	0.01	0.04	0.08	0.18	0.34	0.58	1.01	P.F.	..	20,375+	35.10
9	"	450	51	..	0.020	..	87.3 (7)	..	0.01	0.03	0.18	0.31	0.52	0.82	P.F.	..	19,100−	30.20
10	"	500	68	..	0.015	..	89.2 (7)	..	..	0.03	0.13	0.32	0.59	1.01	P.F.	..	19,100+	30.22
11	200	300	130	113	0.008	0.089	82.3 (6)	..	..	0.03	0.06	0.25	0.58	0.90	P.F.	..	20,375+	28.5
12	"	350	150	128	0.007	0.007	84.3 (6)	..	..	0.03	0.14	0.39	0.77	2.01	P.F.	..	16,575+	32.1
13	"	400	190	152	0.005	0.066	83.4 (6)	0.01	0.03	0.21	0.35	0.75	1.79	P.F.	..	..	14,025−	21.1
14	"	450	260	192	0.004	0.052	85.6 (6)	..	..	0.03	0.12	0.32	0.67	1.39	P.F.	..	11,475	†
15	"	500	360	240	0.003	0.042	83.4 (9)	0.01	0.10	0.27	0.52	0.89	†	..	..	..	..	†

*P.F. Plastic flow.
†Collapsed, owing to internal pipe.

will make it clear that marked segregation occurred only in the castings poured into the moulds heated to 200° C., since the structure shown in Figs. 8 to 13 may be taken as representative of that of the entire casting in each case, segregation having only slightly affected the structure of the castings poured into the moulds at the lower temperatures. The mechanical condition of these castings might be expected to be uniform throughout; results of tests made upon one section should therefore be truly representative of the condition of the entire casting. It is well to bear these facts in mind when considering the test results quoted in Table I.

The positions of the hardness and compression test samples relative to the castings are clearly shown in Fig. 4. It will be obvious, in the light of the above remarks regarding the castings poured into the moulds heated to 200° C., that the test samples removed from the slowly cooled castings could not on any account be looked upon as representative of the condition of the castings as a whole. The test results quoted in Table I for these slowly cooled samples are given only for what they are worth.

If note be taken first of the results of the hardness tests, it will be observed that the Rockwell hardness numbers, which were obtained with a $\frac{1}{8}$-in. ball and a load of 80 kg., are scarcely affected by variations in the pouring temperature of this alloy. These numbers do, however, appear to be influenced by variations in mould temperature, the average Rockwell hardness number for the castings poured into the moulds heated to 100° C. being 2.7 points lower than that for the castings poured into the 0° C. moulds.

The hardness numbers quoted for the castings poured into the moulds heated to 200° C., while not representing the condition of the castings as a whole, are of value in that they give some idea of the resistance of the softest portions of these castings to slowly applied stress and, on this account, may be useful in demonstrating the need of avoiding segregation.

The compression test results are of interest in that they show that the temperature of the mould has but little effect upon the stress required to produce rupture, though it reduces both the stress at which plastic flow first occurs and the percentage reduction in the height of the sample at the time of rupture.

To sum up the results of this investigation, it may be said:

1. That for a given temperature of mould increase in pouring temperature results in an increase in the size of the γ cubes and in a coarsening of the matrix of the alloy.

2. That increase in pouring temperature has less effect on segregation than increase in mould temperature.

3. That mould temperature has a greater effect on the hardness and compressive strength of this alloy than has pouring temperature, increase in mould temperature reducing the resistance of the alloy to slowly applied stresses.

It is difficult to state the above conclusions in terms of cooling or of freezing rates. The means which were adopted for measuring the cooling rates in these experiments were crude. It would have been more satisfactory had it been possible to measure the rate of cooling of the castings, and, in particular, those which cooled most rapidly, at a given temperature. But this could not be done with the apparatus available.

The attempt to correlate the size of the γ cubes and the coarseness of the matrix of this alloy with the times of cooling or with their reciprocals is not completely successful. When the attempt is made one is met with the fact that a marked difference exists between the size of γ cubes in the samples poured into the O° C. mould from 500° C. (Fig. 10) and that of those in the samples poured into the 100° C. mould from 300° C. (Fig. 11). Now the time of cooling in the former case is quite appreciably less than in the latter case, and it might therefore be inferred that the γ cubes in the former samples would be smaller than those in the latter samples. But such is not the case, as reference to Figs. 10 and 11 (Plate I) will show. It may be that the author is wrong in assuming that the reciprocals of the times of cooling are measures of the rates of cooling. It is not improbable, however, that the effects of undercooling need to be accounted for, and these effects cannot be expressed in terms of cooling or of freezing rates. Hence the author has presented his results in terms of temperatures of pouring and of mould rather than in terms of cooling or of freezing rates.

The agreement between the author's findings in respect of this lead-base alloy and those of Hudson and Darley[1] in respect of a tin-base alloy will be appreciated if the conclusions of the latter be quoted here:

1. The size of the γ cubes depends chiefly on the rate of cooling, which is determined largely by the condition of the mould, and is only indirectly (by its influence on the rate of cooling) affected by the casting temperature.

2. The character of the grouping or arrangement of the primary crystallites of the γ constituent is chiefly determined by the casting temperature. The rate of cooling, whether affected by casting temperature or condition of the mould, is confined principally to its influence on the size and shape of individual crystals.

[1] *J. Inst. Metals*, 1920, 24, 361.

III. INVESTIGATION OF A LEAD-BASE BEARING METAL CONTAINING COPPER

The addition of copper or of other metals of high melting point to alloys of the type now under consideration for the purpose of preventing segregation has been suggested. It was thought to be of interest, therefore, to determine the effect of copper on a lead-base bearing metal of about the composition of that dealt with in the last section. An alloy of the following composition, as determined by analysis, was therefore prepared:

	Per Cent.
Lead	82.5 (by difference)
Antimony	11.0
Tin	5.5
Copper	1.0

A series of castings of the dimensions shown in Fig. 4 were produced by pouring at the following temperatures into moulds at 0° C., 100° C., and 200° C.

Mould Temperatures C.	Pouring Temperatures C.	Total Cooling Time Seconds	Reciprocal of Cooling Time
..	300	20	0.051
..	400	25	0.040
..	500	30	0.033
100	300	32	0.031
100	400	34	0.029
100	500	60	0.017
200	300	82	0.012
200	400	152	0.007
200	500	195	0.005

No attempt was made to investigate the mechanical properties of these castings, though it is hoped to pursue this course at a later time.

It was intended at first only to determine the effect of pouring temperature and mould temperature upon the microstructure of this alloy, but the results of the microscopic examination of the castings were so surprising that the author was led to study the electrical resistivity of the alloy in the liquid state.

It may be said at the outset that segregation in the case of this alloy was almost completely eliminated as a result of adding copper. The effect is due, however, not to entanglement of the γ cubes by needles of the tin-copper compound (Cu_3Sn), as was the case in the lead-base alloy, a section of which is shown in Fig. 19 (Plate II) (due to Mr. McBurney), but, in the case of the castings poured at 300° C., to an

effect as yet undetermined by the author,[1] and, in the case of the castings poured at 400° C. and 500° C., to a complete change in structure, which consisted essentially in the replacement of the γ cubes by needles of Cu_2Sb, the purple antimony-copper compound frequently referred to as "Regulus of Venus."

It will be well to deal with the castings in groups. First, let those which were poured at 300° C. be considered. An examination of sections of these castings poured into moulds at 0° C., 100° C., and 200° C., in which there was practically no segregation, if any at all, showed that γ cubes occurred in all cases, these cubes increasing in size as the pouring temperature was raised. At the same time the eutectic became coarser. Figs. 20 and 24 are representative of the structure of the castings poured at 300° C. Due consideration must, of course, be taken of the effect of pouring temperature on the structure of the alloy. Needles of the purple compound were not entirely absent from any of the castings poured at 300° C., though they were relatively few in number. In the case of the casting poured into the mould at 0° C. such needles as were present could only be distinguished from the eutectic antimony by their colour. In Fig. 24 (Plate III), which is a photomicrograph of a section of this casting at a magnification of 500 diameters, one such needle is present. It lies at an angle of about 55 degrees to the lower edge of the photomicrograph, and intersects this edge at a point about 0.5 in. distant from the left-hand corner of the print.

In the castings poured at 400° C. but few cubes were to be found. They were not entirely absent, but were rare, save in the casting poured into the mould at 200° C., which cooled somewhat more slowly than the other two. In place of cubes, needles of the purple compound appeared, as may be seen in Fig. 21 (Plate III). These needles appeared to be quite unaffected by the temperature of the mould—that is to say, that some quite large needles occurred in the castings poured into the 0° C. mould, and some quite small ones in the castings poured into the 200° C. mould. The eutectic, however, was affected as in the case of the previous castings—it became coarser in structure as the mould temperature increased.

The castings poured at 500° C. (Figs. 22, 23 and 24, Plate III) were possessed of structures which were on the whole similar to those of the castings poured at 400° C. The eutectic was found to be affected by mould temperature as in the previous cases. The purple needles, however, were far more uniform in size and distribution. Again mould

[1]The effect may be related in some way with that of copper in transforming the γ cubes, which is referred to on p. 153 and is shown graphically in Figs. 28 and 29 (Plate IV).

temperature appeared not to affect their dimensions. Only in the casting poured into the high-temperature mould were cubes of the γ constituent present in such numbers as to be noticeable.

A photomicrograph, at a magnification of 500 diameters, of the structure of the casting poured at 500° C. into the mould at 200° C. is shown in Fig. 25 (Plate III). It serves to make clear the distinct difference in colour between the γ cubes, the antimony of the eutectic, and the needles of "Regulus of Venus."

The above results were so surprising that the author felt that some error must have been made while casting the alloy; that segregation had occurred in the ladle, and that the castings differed in composition on this account. To test this out the casting which had been poured at 300° C. into the 200° C. mould was heated to 500° C. and poured into a mould at room temperature. The structure of the alloy after this treatment is shown in Fig. 26 (Plate IV). The γ cubes have practically disappeared, and in their place needles of the purple compound have been generated.

A test was then made to determine the effect of heating a sample of the alloy to 500° C., then allowing it to cool slowly to 300° C., and finally pouring it into a mould at room temperature. The structure of the casting obtained under these conditions is shown in Fig. 27 (Plate IV). It will be seen that this structure is a compromise between those depicted in Figs. 20 and 22 (Plate III). The replacement of the purple needles which characterize the alloy when poured at 500° C. (Fig. 22) by the white cubes which characterize the alloy when poured at 300° C. (Fig. 20) is in progress, but an equilibrium state has not been even approximately reached.

These remarkable results could, the author felt, be explained only by assuming that an intermetallic reaction occurred in the liquid alloy at some temperature between 300° C. and 400° C. This reaction might be expressed by the following equation:

$$2Cu + SnSb = Cu_2Sb + Sn.$$

Now the continued existence of the compound Cu_2Sb in the liquid state has been admirably demonstrated by Bornemann and his collaborators,[1] but the author has been unable to discover evidence of the continuity of the γ constituent of the antimony-tin system in the liquid state. It is not, however, difficult to conceive of the latter compound existing as an entity in the liquid alloy now under discussion and reacting with copper in solution in the melt to form the purple compound, Cu_2Sb, in accordance with the equation proposed above. It would be expected that such a reaction, were it to occur, would have

[1] *Metallurgie*, 1912, 9, 473.

an effect on the temperature coefficient of resistivity of the alloy in the liquid state, and in order to test this the author made numerous experiments to determine the electrical resistivity of this alloy in a molten condition.

In the earlier experiments the author employed small U-tubes of Pyrex glass to hold the liquid alloy. The first experiment with this apparatus was entirely successful in so far as the heating curve was concerned, but on cooling the alloy the tube furnace was inadvertently opened at one end, and the rate of cooling of the thermocouple, which was placed between the two arms of the U-tube, was made greater than that of the alloy and the true resistivity-temperature relationship was destroyed. It should be noted, however, that the heating curve was characterized by an inversion at a temperature above the liquidus for the alloy. The temperature of this inversion was 334° C.

On thinking over the results of this first experiment it became

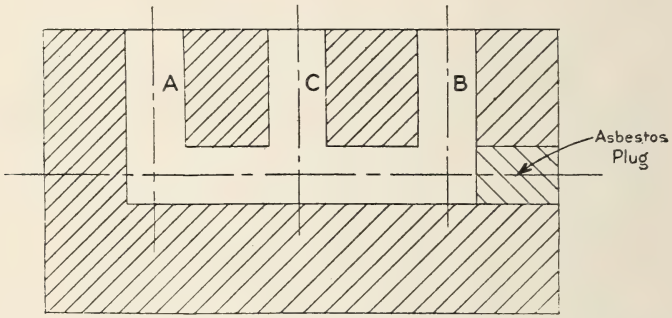


FIG. 5.—Magnesite Brick prepared for Reception of Alloy (Resistivity Measurements).

clear to the author that the inversion observed might have been due to the magnetic change in the nickel wires which were employed as leads for conveying current, etc., to and from the melt. It was decided, therefore, to replace the nickel wires by copper, it being felt that the solubility of copper in the alloy at the temperatures used in these experiments would be so small as not to affect the composition of the alloy during the time occupied in making a test. Numerous trials were now made, using Pyrex glass tubes of various sizes and copper leads. All, without exception, failed, owing to rupture of the tubes during heating.

Recourse was then had to a device in which dipping electrodes of steel were used. The alloy was melted in a graphite crucible. Into the molten alloy two flat steel electrodes, insulated from one another at their points of support, were dipped. Using this arrangement it was possible to obtain full confirmation of the transformation in the liquid alloy, but continuous observations throughout the freezing

range were found to be out of the question, owing to the fact that a pipe invariably formed in the space between the electrodes.

Satisfactory results were finally obtained by using a very simple method, which the author later found had been used by Bornemann and his collaborators (*loc. cit.*). A magnesite brick was drilled in the manner shown in Fig. 5 (p. 13). The horizontal hole was then plugged with asbestos and the other holes filled with alloy. Electrodes of copper

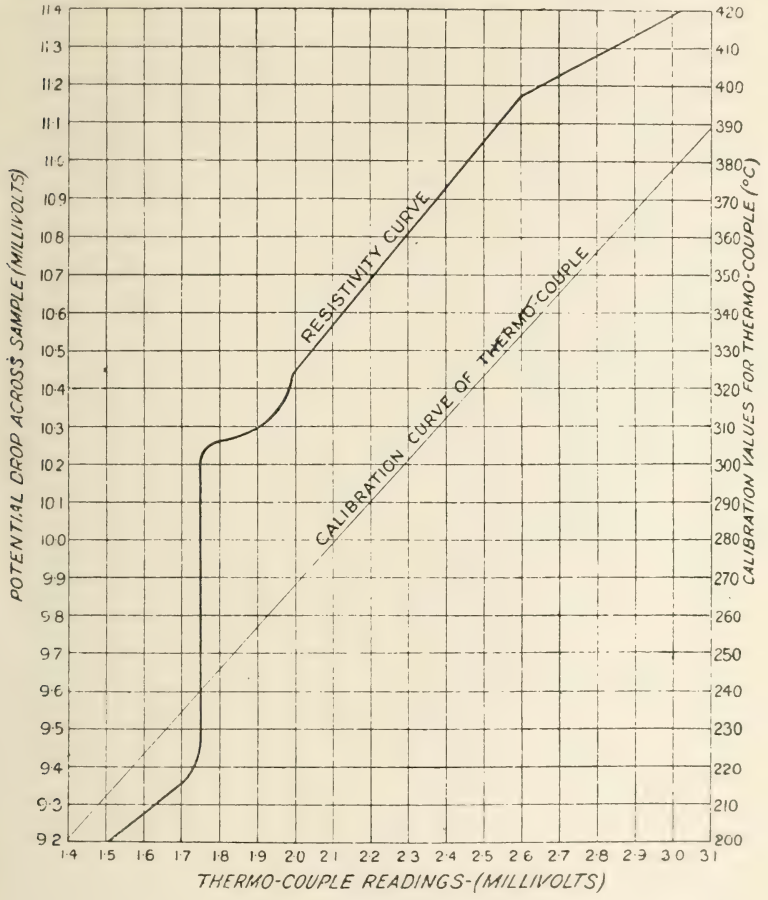


FIG. 6

were introduced into the vertical holes A and B, and a thermocouple, sheathed in a Pyrex glass tube, was placed in hole C. Using this device the author was able to obtain perfectly consistent results. The form of the resistivity-temperature curve obtained by him is shown in Fig. 6. No attempt was made to determine actual values for the resistivity of the alloy.

Reference to Fig. 6 will make it quite clear that a radical change in this alloy occurs at 334°C., *i.e.*, in the liquid alloy. The author is of the opinion that this change is of the character described above—that an intermetallic reaction takes place in the liquid alloy at 334° C. Whether the copper in solution in the melt reacts with the γ constituent

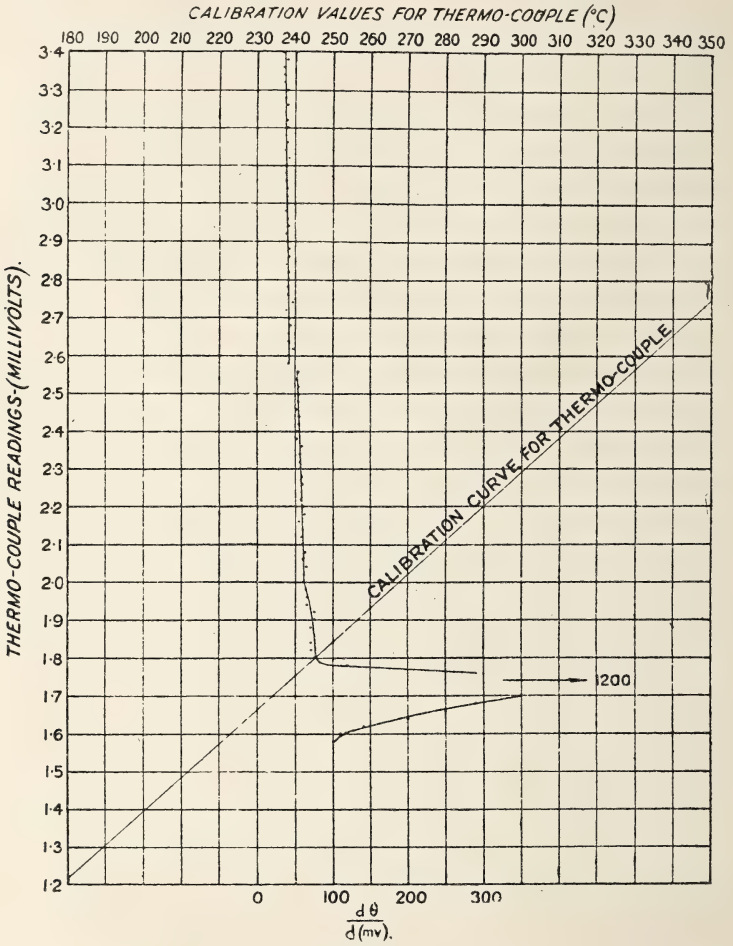


FIG. 7

to form Cu_2Sb, or whether it reacts with antimony in the melt to form the purple compound, is matter for debate at the moment. There being no clear reason for doubting the existence of SnSb in the liquid state, the former of the two possibilities appears the more likely.

The intermetallic reaction also appears to affect the thermal characteristics of the liquid alloy. The change in heat content at 334° C.

is, in fact, quite noticeable. To demonstrate this a cooling curve for the alloy is given (Fig. 7), reference to which will make clear the nature of the change in terms of the heat content of the alloy.

In conclusion, a word may be said regarding the effect of small additions of copper on the structure of these alloys. Figs. 28 and 29 (Plate IV) represent the structures of the upper sections of castings of the alloy referred to in the second section of the paper, which were inadvertently contaminated as the result of stirring the melt in the ladle with a carbon rod that had been used previously in stirring the copper-bearing alloy. The carbon rod not having been cleaned, a small portion of the copper-bearing alloy was introduced into the melt. Fig. 28 represents the top section (segregate) of a casting poured at 400° C. into a mould at 200° C. and should be compared with Fig. 15 (Plate II), which represents a similar section in an uncontaminated casting; Fig. 29 (Plate IV) shows the top section of a casting poured at 500° C. into a mould at 200° C. and should be compared with Fig. 17 (Plate II). The presence of tiny needles of Cu_2Sb is evident in Fig. 29 (Plate IV).

The author does not feel competent to attempt an explanation of the web-like structure of the large cubes, but that the presence of copper in the alloy accounts for their remarkable appearance he believes to be true. It is not altogether impossible that this effect of copper may have some indirect connection with the influence of this element in controlling and preventing segregation.

IV. SUMMARY

The results of this investigation may be summarized in the following terms:

1. Within the limits of these experiments the replacement of lead by antimony increases the resistance of these alloys to compression. The hardness of these alloys is subject to a like increase (*cf.* the author's previous work).[1]

2. Within the limits of these experiments the replacement of tin by copper increases the resistance of these alloys to compression. The hardness, however, is scarcely affected by the substitution.

3. Mould temperatures exert a more powerful effect on the alloys referred to in the paper than do pouring temperatures.

4. For a given temperature of mould increase in pouring temperature results in an increase in the size of the γ cubes and in a coarsening of the matrix of the copper-free alloy.

5. Increase in pouring temperature has less effect on segregation than increase in mould temperature.

[1] *J. Inst. Metals*, 1918, 19, 151.

6. Increase in mould temperature causes a reduction in the resistance of these alloys to slowly applied stresses. The copper-bearing alloy has not been fully investigated in this respect.

7. Addition of copper has an important effect on the structure of these alloys.[2]

8. There is evidence for the belief that an intermetallic reaction occurs in the copper-bearing alloy investigated by the author in the liquid state at 334° C.

APPENDICES

1. A point which may be of interest in connection with the manner in which the copper-bearing alloy behaved when in process of preparation for micro-examination is the following: The samples in which the γ constituent was present were easier to finish than those containing the copper compound. In preparing the samples for micro-examination the final polish was given by means of the finger, using Glosso liquid metal polish as a polishing medium. When polishing lead-base alloys this medium forms a black paste. This paste it was found was quite readily removed from the samples of the alloy which contained no copper, was somewhat less easily removed from the samples of the alloy which did contain copper, but in which the γ constituent was present, and was only removed with difficulty from the samples of the latter alloy which contained Cu_2Sb. The only satisfactory means of removing the tenacious paste which formed on these samples was to wash them thoroughly in ether. It was found impossible to use caustic soda solution for this purpose, as could be done in the case of the copper-free samples. It should be noted that no attempt was made to differentiate between different cans of polish, variations in which may, of course, have had some influence in this connection.

2. The coexistence of Cu_3Sn and of Cu_2Sb in a tin-base anti-friction alloy has been noted by the author. A slowly cooled ingot of the following composition:

	Per Cent.
Tin	91
Antimony	4½
Copper	4½

was examined microscopically. It was found that segregation of the primary constituents had occurred. These constituents had, however, collected at the bottom of the ingot, not at the top. The photomicrograph of Fig. 30 (Plate IV) will give some idea of the structure of the bottom section of the casting referred to. It will be seen that both cubes and needles are present in the section. What is possibly of par-

[2] *Vide* also *Nature*, 1925, 115, 382.

ticular interest is that the needles are cored. On account of the difficulty of distinguishing between the two phases present in the needles shown in Fig. 30 the author has prepared the photomicrograph of Fig. 31 (Plate IV), in which the cored sections (Cu_2Sb) of the needles have been blackened. The central portions of the needles were found to be purple in colour—they apparently consisted of the antimony-copper compound (Cu_2Sb); the outer portions of the needles were white—they apparently consisted of the copper-tin compound (Cu_3Sn). The question arises, Why did the constituents here collect at the bottom of the ingot? One is tempted to assume that the copper compounds must be more dense than the γ constituent and than the matrix of the alloy. This greater density may in part account for the effect of copper in reducing the segregation of the constituents in these anti-friction alloys.

EXPLANATION OF PLATES

Plate I

Fig. 8. Top section of copper-free alloy casting poured at 300° C. into mould at 0° C.
" 9. " " " " " " 400° C. " " "
" 10. " " " " " " 500° C. " " "
" 11. " " " " " " 300° C. " " 100° C.
" 12. " " " " " " 400° C. " " "
" 13. " " " " " " 500° C. " " "

The structures shown in Plate I photomicrographs are representative of that of the entire casting.

×100 unetched

Plate II

Fig. 14. Top section of copper-free alloy casting poured at 300° C. into mould at 200° C.
" 15. " " " " " " 400° C. " " "
" 16. Middle " " " " " " " " "
" 17. Top " " " " " 500° C. " " "
" 18. Bottom " " " " " " " " "

×100 unetched

" 19. Section of bearing metal showing effect of Cu_3Sn needles in preventing rise of SnSb cubes through melt. ×150.

Plate III

Fig. 20. Section of copper-bearing alloy poured at 300° C. into mould at 0° C. ×150
" 21. " " " " " 400° C. " " 100° C. ×150
" 22. " " " " " 500° C. " " 0° C. ×150
" 23. " " " " " " " " 200° C. ×150
" 24. " " " " " 300° C. " " 0° C. ×500
" 25. " " " " " 500° C. " " 200° C. ×500

Plate IV

Fig. 26. Section of copper-bearing alloy (i) poured at 300° C. into mould at 200° C. then (ii) re-melted and poured at 500° C. into mould at room temperature. ×150.
" 27. Section of copper-bearing alloy (i) heated to 500° C. then (ii) cooled slowly to 300° C. and poured into mould at room temperature. ×150.
" 28. Structure of upper section of alloy contaminated by copper—to be compared with Fig. 15 (Plate II). ×150.
" 29. Ditto ditto Fig. 17 (Plate II). ×150.
" 30. Co-existence of Cu_3Sn and Cu_2Sb in the same section. ×100. Etched with silver nitrate.
" 31. Photomicrograph to make clear Fig. 30. ×100. Etched with silver nitrate.

Plate I

Fig. 8.

Fig. 9.

Fig. 10.

Fig. 11.

Fig. 12.

Fig. 13.

Plate II

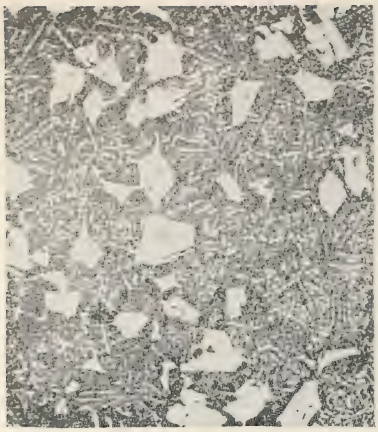


Fig. 14

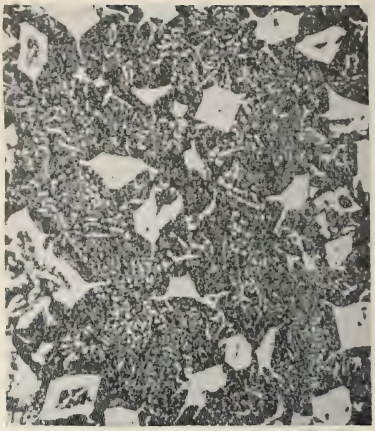


Fig. 15.

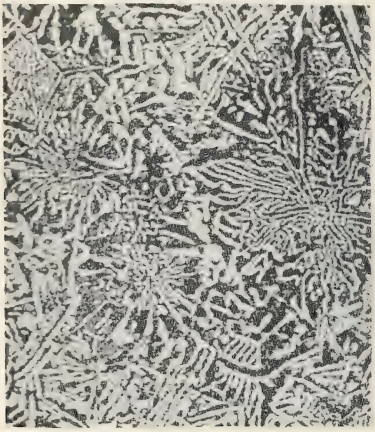


Fig. 16.

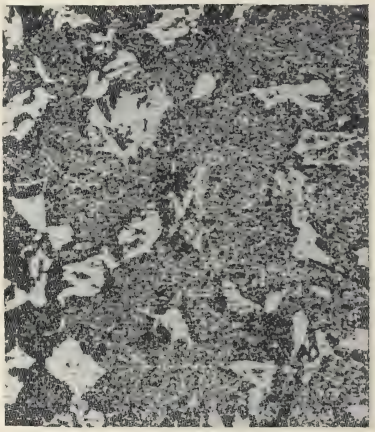


Fig. 17.

Fig. 18.

Fig. 19.

Plate III

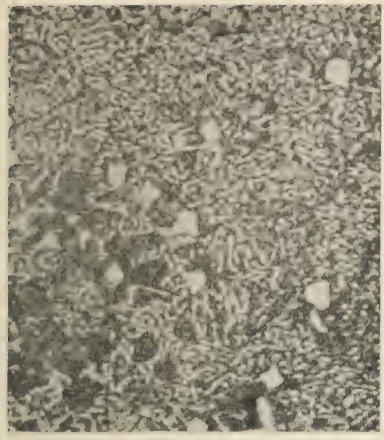


Fig. 20.

Fig. 21.

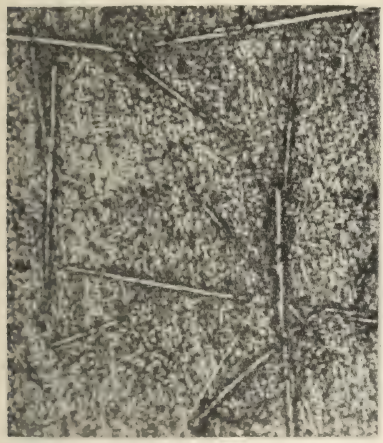


Fig. 22.

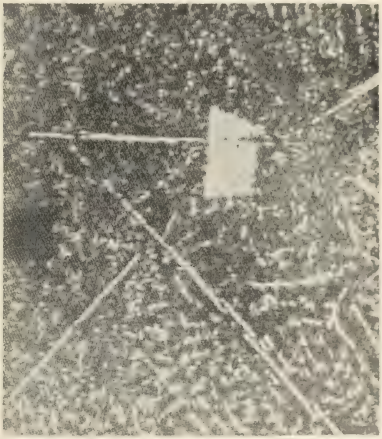


Fig. 23

Fig. 24.

Fig. 25.

Plate IV

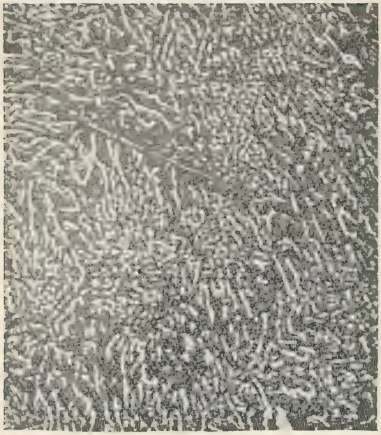


Fig. 26.

Fig. 27.

Fig. 28.

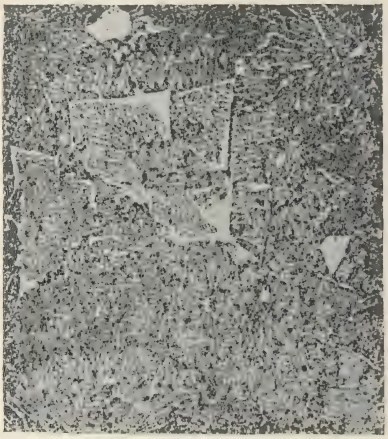


Fig. 29.

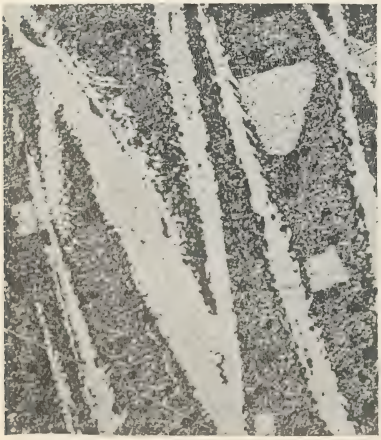


Fig. 30.

Fig. 31.

INTAKES FOR POWER PLANTS

Including a Description of Experiments and Results on a Large Scale Model

By Robert W. Angus, *Professor of Mechanical Engineering*

The purpose of this paper is to set forth the desirable features of intakes placed in rivers or other bodies of water for supplying water for hydraulic turbines and other equipment. The paper makes special reference to protection against ice and other large floating substances. It includes a description and discussion and conclusions with reference to an extensive set of experiments made by the author at Niagara Falls, Canada, on a large model of the Niagara River, their immediate object being the design of a suitable intake for the Queenston hydro-electric plant.

The construction of a water intake for a power plant or waterworks is frequently simple, where the volume of water taken in is relatively small and free from objectionable floating material, but in many water and steam power plants and in some waterworks installations the problem is a very serious one. The difficulty of the problem depends on the volume of water to be taken in, the depth below the surface at which the intake may be placed, the velocity of the water in the source of supply, and on the amount of floating material present. Where there is much ice the design must be very carefully worked out to be effective.

In the northern parts of the United States and in Canada, ice produces one of the most serious troubles and has been the cause of more or less frequent shutdowns in plants, and has also caused serious damage to the turbines and machinery. Many illustrations of this might be given, but the great power developments on the Niagara River are typical, these being mainly located where the water is shallow, the current moderate, and the volume of water drawn in very large. This river carries vast quantities of ice at certain times of the year, since in addition to what forms in the river itself, there is the accumulation from Lake Erie, the

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ice from which, with a strong wind, may be blown over against one shore or the other, and thus forced into the power plants on that side of the river. In this instance the plants are closed down at times for short periods due to ice blocking the intakes.

The photographs shown herewith give some idea of what has happened in these cases, Fig. 1 indicating an ice condition on the Niagara River at Hog Island.

This paper has in view primarily the design of an intake to avoid drawing in ice, and usually if ice can be avoided other floating substances not in suspension are likely to be avoided, although the plans investigated would not serve in case of sand or small stones.

FIG. 1. Mouth of Welland River, Showing Ice Field Extending from Niagara River; Lighthouse on Hog Island

DESIRABLE PROPERTIES OF AN INTAKE

An intake must be simple in form and easily constructed. This is self-evident when it is remembered that they are used under water and frequently must be constructed without unwatering. Further, the danger of blocking up increases as the intake becomes more intricate in form, and the difficulty of cleaning is also increased.

The intake must be thoroughly reliable and positive, even to the extent of sacrificing some efficiency for certainty of operation. It is very necessary that an intake should never fail to supply the desired volume of water, and it is therefore better to have a small amount of ice and debris enter it, if necessary, a good part of the time under part loads, than to make the design so complicated as to render it liable to choke up when

the draft is heavy. On the whole, an intake that functions properly under full load will have little chance of drawing in debris at other times.

The intake should have a large factor of safety on operation—greater, indeed, than other parts of the plant, partly because of the lack of knowledge of effective design, as demonstrated by the failure of so many intakes under critical conditions. On the other hand, money may be needlessly wasted by making large and ineffective designs. The loss of head in the intake should be small, as it produces a decrease in the effective head on the plant.

A large factor of safety naturally suggests an intake covering a considerable area, but it must be kept in mind that the larger the area occupied, the greater the field of ice from which the intake may draw. It is also well known that, while the larger area would tend to decrease the volume of water drawn in from each square foot of surface, yet it may follow that an imperfect design may be little benefited by an increase in size, since the draft may not be equally distributed over the area covered by it.

This statement is evident to any one observing the action of intakes, for there are many cases where the intensity of draft varies enormously over the area covered by the intake, and where the distribution is far from uniform. In fact, it is one of the most difficult things in hydraulics to arrange for a uniform draft of water over a prescribed inlet area.

Where water in proportionately large quantities is drawn from a flowing stream, such as a river, there will be a natural decrease in velocity below the intake, and this must be compensated for in some manner or else the intensity of the floating ice or debris will increase just over the intake, thus making the danger more serious. Manifestly if any change in the velocity of the water in the river takes place at the intake, it should be an increase.

The most obvious way of keeping up the velocity would be to make the river shallower in passing the intake, but if this is done to any great extent, the tendency is to divert the water away from the intake over toward the center of the stream, and thus defeat the very object in view. If compensation is attempted by narrowing the river with a diverting wall or dam, there is danger of concentrating shore ice above it and of forming a pool of dead water with floating debris above the diverter and close to the intake.

It is clearly impossible to avoid drawing in some ice or debris, since at times these may be found at all depths of the river or other source, but the minimum of foreign matter will be taken in where the water is drawn from the bottom of the source. If the intake is designed to

function in this way, then some scheme must be devised to deal with logs, etc., rolling along the bottom, and provision must be made for taking them through the intake, or for removing them from it, if it is not possible to make them pass over it.

If the intake openings are not large, then foreign substances will stick in them and will have to be removed by divers or some others means, often a very difficult matter.

The distance from which a floating mass will be drawn into an intake depends very largely upon the velocity of the water entering the latter, hence, unless the intake is in very deep water, the velocity of the entering water must be low. Here again attention is called to the fact that this condition is not necessarily met when the quotient of the volume of the water to be taken in divided by the area of the intake is small, since the velocity on at least half of the intake may be much higher than this quotient.

The foregoing considerations have been set out at some length so that a clear conception of the problem may be established. A number of the principles stated have been fairly well understood for years, and yet the fact is that many intakes are unable to meet a severe test such as comes at an unfavourable time. Examples of inadequate designs are not wanting, and one well-known case may be cited where the designer did not realize the value of low velocities, as his design shows a mean velocity of entry of the water of 4.5 ft. per sec. and it fails to handle the ice with any satisfaction, while the plant suffers considerably from shutdowns.

EXPERIMENTAL AND RESEARCH WORK ON INTAKES

Unfortunately very little experimental work has been done on intakes, or at least little is available, and consequently former mistakes are being repeated. The experiments about to be described may therefore prove of interest, not because they are particularly exhaustive, but because they indicate some of the causes of failure and may prove helpful to those facing this important problem.

The experiments referred to were made by the author in connection with the large development recently built at Niagara Falls by the Hydro-Electric Power Commission of Ontario, Canada. As is well known, the intake for this development is at the mouth of the Welland River, which is some two miles above the Horseshoe Falls; the river surface at this point is only a slight distance below the level of Lake Erie, and vessels may navigate from Buffalo down the river to the village of Chippawa, which is situated on the Welland River.

The level of the Niagara River at this point varies from 558 ft. to 561 ft. above mean sea level, and the width of the river is slightly over one mile. At the intake location the depth of the river at 600 ft. from shore was only 15 ft. with the water at El. 561 ft. and 12 ft. at El. 558 ft., and the depth rather decreases further out. At a point opposite the mouth of the Welland River the measured velocity was 4.2 ft. per sec. and the volume of water passing down the Niagara River within a distance of 600 ft. from shore varies from 25,000 cu. ft. per sec. when the river is at El. 558 ft. to 32,000 cu. ft. per sec. when the river is at El. 561 ft. The corresponding quantities for 1200 ft. are 45,000 and 59,000 cu. ft. per sec., respectively.

At the time the investigation was in progress it was the intention to draw 15,000 cu. ft. per sec. from the Niagara River for the plant at Queenston, but in view of the fact that a safety factor was desired, the experimental work was planned with the possibility of larger drafts of water than the above, and, indeed, later developments have shown that the draft will in time exceed the 15,000 cu. ft. per sec. It was not desired to have the intake extend further out from shore than was necessary, partly on account of difficulties of construction in the river.

If the intake was not to extend out more than 600 ft. from shore, the problem confronted was that of drawing from a river 12 to 15 ft. deep, having a velocity of 4.2 ft. per sec., heavily burdened with ice at certain seasons, approximately one-half the available water in this width without causing serious ice trouble in the plant; and even if the intake extended twice as far, the draft would be about one-third of the supply. Extra care was also necessary because the water was to be taken down an open canal 13.5 miles long, without any means of disposing of ice along the route.

In view of the importance of the problem and the lack of information, a model of the river and canal was decided on, and fortunately a space was available at the Dufferin Islands, Niagara Falls, Ontario, where it was possible to build to a scale of one-twentieth full size, a model of the Niagara River out to about 2000 ft. from shore, and for a length of 4000 ft., there was also room to include 2800 ft. of the Welland River. The model was so laid out that the intake site would be at about the center. The supply of water for the experiments was introduced at a distance of 170 ft. above the beginning of the model of the bed.

In order to make it true in every way, the bed of the model was constructed to agree with what was known of the contours of the beds of the Niagara and Welland rivers, and very great care was taken in the the grading, stakes being set up every 10 ft. in each direction. Gages

were also set in the model to represent the river stage, and it will be noted that since the experiments were made for El. 558 ft. to 561 ft. of the river, the depth of water in the model was only from 7.2 to 9 in., and this small depth necessitated the very greatest care in the whole scheme.

LAWS FOLLOWED IN USING THE MODEL

In using the model it was necessary to determine the scale relations for the discharge and velocity from the physical dimensions. While there is no absolute information on the point, the laws of hydraulic similarity have nevertheless been fairly well established, the experience shows that models will represent the actual results with great accuracy,[1] those obtained with model turbines, etc., being remarkable in their correspondence with the full-size machines. In this case the physical dimensions were reduced to the adopted scale of one-twentieth, which made the slope of the water surface and bed in the model the same as that in the river. The cross-sectional area of the water was therefore reduced in the ratio of $1 : (20)^2$ or $1 : 400$.

Since the bottom resembled the actual river bed in contour, and since the roughness of the bottom was reduced in about the same proportion, it was thought that the coefficient in the Chézy formula, $v = c\sqrt{rs}$, would be the same in the model as in the actual river; in other words, the decrease in Kutter's n would about compensate for the decrease in r, so that the velocity v would vary as the square root of the hydraulic radius r. On this basis the velocity in the model should be reduced in the ratio $1 : \sqrt{20}$, and this was the general ratio adopted, although the model experiments were made at several rates of discharge of the river and hence were not vitally affected by inaccuracy in this rule. The discharge in the model should thus be reduced in the ratio $1 : 400\sqrt{20}$ from that in the corresponding part of the river, giving for El. 561 a discharge of 52.56 cu. ft. per sec. and for El. 558 ft. a volume of 39.60 cu. ft. per sec. to be passed down the model river.

The desired volume of water was admitted to the model over an 18-ft. weir, Figs. 2 and 3, which was 280 ft. above where the intake was placed, and by suitable arrangement of stones and obstructions the water was forced to spread over the entire model in the same proportion as in the river. While adjusting and distributing the volume, the river stage was controlled by a dam below the intake, and after some

[1] See paper by B. F. Groat, Trans, A.S.C.E., vol. LXXXII, p. 1138.

experimenting the adjustment was made so as to represent actual conditions.

In Fig. 2 will also be seen the model of the bed of the reconstructed

FIG. 2. General View of Model with Improved Welland River in Foreground and Niagara River in Background

FIG. 3. Supply Pond on Right with 18-ft. Weir Feeding the Model on the Left

Welland River with the model intake at its mouth where the men stand, and a 9-ft. weir to measure the quantity drawn off in the intake, the

control of this quantity being effected by the slats shown just above the weir.

The arrangements thus made it possible to send any desired volume of water down the river, to adjust its gage height independently, and to draw off on the intake any desired volume.

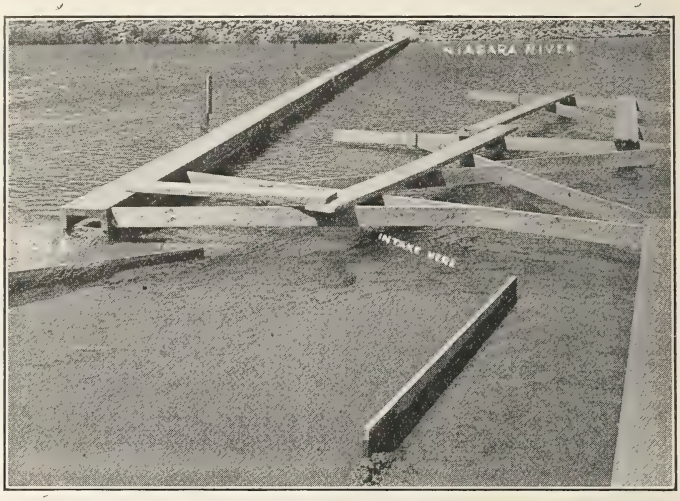


Fig. 4. Metering Bridge and Structure to Allow Measurements to be Made on Intake which is in Place

LEAKAGE OF WATER FROM THE MODEL

Leakage was a matter of great concern, and no doubt some did occur owing to the nature of the materials, although precautions were taken to prevent it. In order to have a check on this, as well as to check the desired distribution of the velocity in the bed, a current-metering station was arranged just below the intake to correspond to a section of the river at which discharges had been measured. This station was made in the form of a bridge, Fig. 4, across the main channel to the left of the men shown on Fig. 2 (see also Fig. 5).

It will thus be seen that the discharge by the 18-ft. weir should equal that by the current meter and the 9-ft. weir combined, and a number of comparisons were made from this standpoint in the course of the experimental work. The following are some of the results obtained.

Measurements by			Total of last
48.25 c.f.s.	0 c.f.s.	49.1 c.f.s.	49.1 c.f.s.
48.25	0	49.2	49.2
49.0	5.65	45.2	50.85

Many of the results thus agreed quite well, showing little leakage, although others were not so accurate.

METHOD OF CARRYING OUT THE EXPERIMENTS

The first procedure was to get a distribution of water over the model similar to that existing in the Niagara River before the intake was placed in it, and the model was therefore first made without any intake,

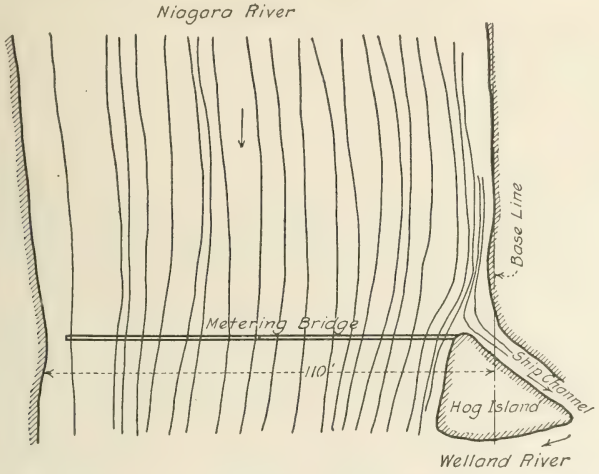


Fig. 5. Paths of Deep Floats in Model River Channel as it Originally Existed Before Any Intake was Constructed.

but with the original river with Hog Island, the ship channel, and all details as shown in Fig. 5. By the use of the current meter on the bridge and also by the use of floats, the proper distribution was effected through the placing of stones and obstructions just below the 18-ft. weir and also by adjustment of the dam below the intake, the final results being as shown in Fig. 11, the actual conditions agreeing with the model fairly well.

The floats in this case were bottles sunk to a depth of about 2.5 in., and the path and velocity of each float were taken by stretching wires across the model at 25-ft. intervals, each wire having graduations on it 5 ft. apart. A float was then placed in the channel at the desired distance from shore and 25 ft. above the first wire, and as the bottle

passed under the first wire, one observer signalled and a second observer on the bridge noted the time on a stop watch, also noting the distance out from shore and plotting the point on cross-section paper, containing a plan of the river, at the same time; the same procedure was followed with all of the wires. In this way five points were plotted on the path of each float, also the approximate intermediate path between wires, the field plotting much decreasing the chance of error.

Having thus adjusted the conditions to correspond to those in the Niagara River, the channel was unwatered and the intakes built into place. During the two seasons thirty-five models were experimented on, covering the different types with their various modifications. In placing these intakes, the area to be covered by each was staked off and great care was taken not to disturb the remainder of the river bed. It is not practicable to give full information here on all the intakes used, nor complete details of the results obtained, but the method was the same in all of them, and the first one will be described more fully than the others.

The primary object in the experiments was to get an intake which would avoid taking in a troublesome amount of ice and debris; and hence it was desired to know what effect would be produced on the stream lines of the river, how much tendency there was for the intake to disturb the conditions at a greater distance from shore than it extended, and what tendency there was to draw in floating ice and debris as well as substances floating below the surface. The loss of power due to friction, etc., involved in the design is also important, and it is, of course, desirable to keep the cost down to the lowest figure consistent with good design.

To study the effect of the intake on cakes of ice, floats made of oak blocks of different sizes were used, these being heavy enough to float about 90 per cent. submerged. Bottle floats were used to arrive at subsurface effects and these were sunk to different depths to suit the case. The paths of the floats were plotted in the way already described, but in the vicinity of the intake extra wires were used and more detailed information on the paths of the floats was obtained. Distribution of the flow was also determined by the use of the current meter, this being also used to find the velocity at the different points around the intake. In addition to these data, the actual directions of the water particles were determined in many cases by means of a light string attached to the lower end of a stick, to the upper end of which a protractor was attached.

TYPES OF INTAKES TRIED

In general there were three types of intakes experimented on, and for want of a better nomenclature these may be briefly referred to as (*a*) open intakes, (*b*) closed intakes, and (*c*) combined intakes. In this paper open intakes are those having no physical structure to separate the surface water in the river from that in the power canal; that is to say, boats not drawing too much water could pass freely from the source of supply into the power canal right over the intake. By closed intakes is meant those where the water from the source of supply passes through a closed tube of some length on its way to the power canal; such intakes have a series of tubes opening at one end into the main river or source and into the power canal at the other, and all water

Fig. 6. View of Intake *A* Looking from Power Canal Toward Niagara River; Model Unwatered.

entering the latter must pass through the tubes. Combined intakes are referred to as those with tubes where the water enters along a considerable length of the tube, but like the closed type a curtain wall of some kind cuts off the surface river water from the power canal.

The first intake was entirely an open one of a type invented by Mr. B. F. Groat, and is shown in Figs. 6 and 7 in place. Mr. Groat has stated[1] in a paper his ideas on an intake, and as it was worked out in this investigation it consisted of four open slots or fingers sunk

[1]Trans. A.S.C.E., vol. LXXXII, p. 1138.

in the bed of the river and discharging into a single channel at the entrance to the power canal. The sides of the fingers were made of plank and were vertical, and the bottom of the river was built with a rising gradient between these fingers and thus compensated for the water drawn off by the intake; the bed of the model just below the last slot was therefore higher than just above the first one.

The set of observations taken on the first intake operating under one condition—not, however, that for which this was best suited—is given in Fig. 8, the figures denoting the velocities in feet per second by the current meter and the arrows giving both the direction and sense of the particles. The direction indicator proved much more sensitive

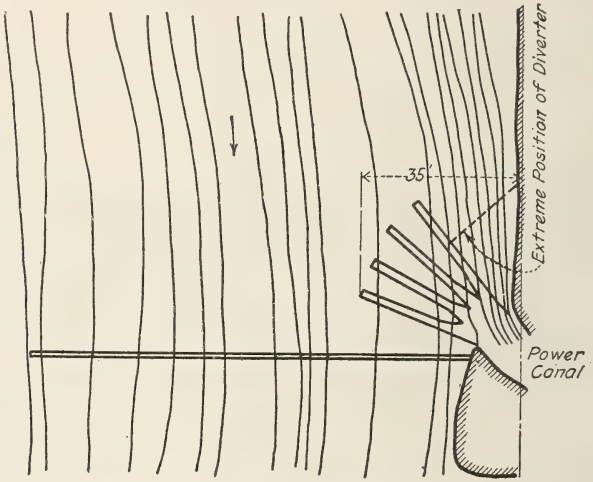


Fig. 7. Paths of Deep Floats in River with Intake *A* Drawing 8.5 cu. ft. per Sec.; River Gage, 560.5 ft.

than the current meter. In each case, of course, the water drawn off by the intake was measured, as well as the flow in the river and its height.

With this particular intake, experiments were made with some variations in the slots, and with diverters or walls running out from the shore above the intake to various distances; but both shallow and deep floats went into the canal in large numbers, particularly those nearest the shore, and the intake in this form did not give satisfaction. The author does not wish to be misunderstood in this matter, for Mr. Groat states that he was able to keep out floating materials in experiments he tried. Probably some other proportions or dimensions than those used

were necessary; but it did not seem advisable at the time to continue work on it.

Modifications of this were made, these broadly taking the form of a curtain wall reaching down below the water surface, so that floating matter had to pass under a submerged wall before entering the canal, the bottom of the wall corresponding to El. 548.5 ft. This was along the lines adopted in many earlier intakes, but proved of little value, as

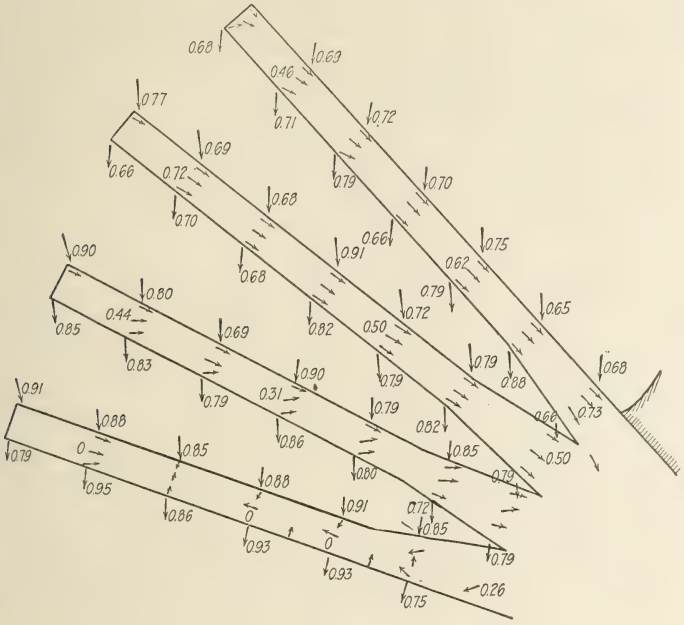


Fig. 8. Intake *A* in place. Diagram Showing Method of Studying the Action of an Intake. Figures Denote Velocities and Lines Show Direction of Currents.

block and bottle floats coming close to the wall invariably went down under its face into the canal. This intake was then modified by the addition of a submerged horizontal platform 28 in. wide in front of the wall, as shown in Fig. 9, but again, while this proved helpful, it had the objection that eddies formed at *A*, and there was also relatively dead water near the vertical wall. The block floats had a tendency to bunch over the intake, but there was clear evidence of a distinct improvement over the vertical wall alone, and the volume was fairly uniformly distributed over the area of the opening. The intake loss in this case was

increased and amounted to 0.56 in. when drawing 8.05 cu. ft. per sec., which would correspond to 14,400 cu. ft. per sec. in the actual case.

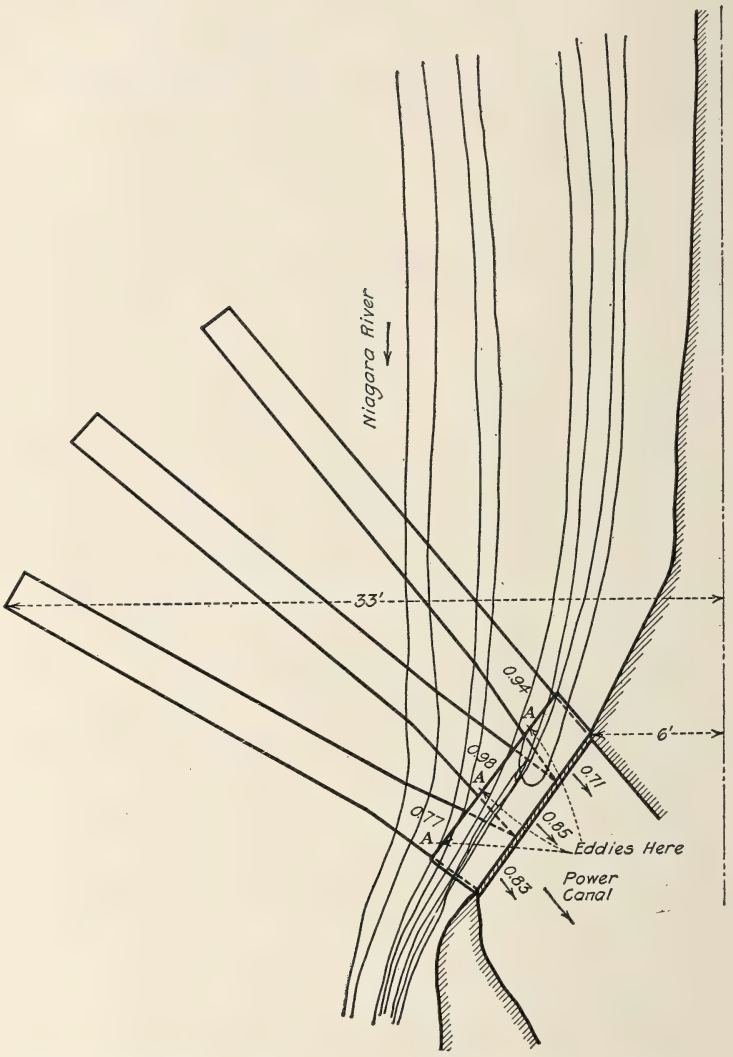


Fig. 9. Intake *B* Drawing 8.05 Cu. Ft. per Sec.; River Gage, 560.6 Ft. Figures Give Velocities. Loss, 0.56 In.

This suggested that a proper design of cover might produce the desired results provided that eddies could be avoided and the loss was not too large. Naturally the experimental season was short, and it was

not possible to digest the results at leisure, so that the changes to be made had to be decided upon quite rapidly. In the next intake, therefore, the cover was extended out further, with the result that the floats decreased in speed as they went down over the intake and a number of

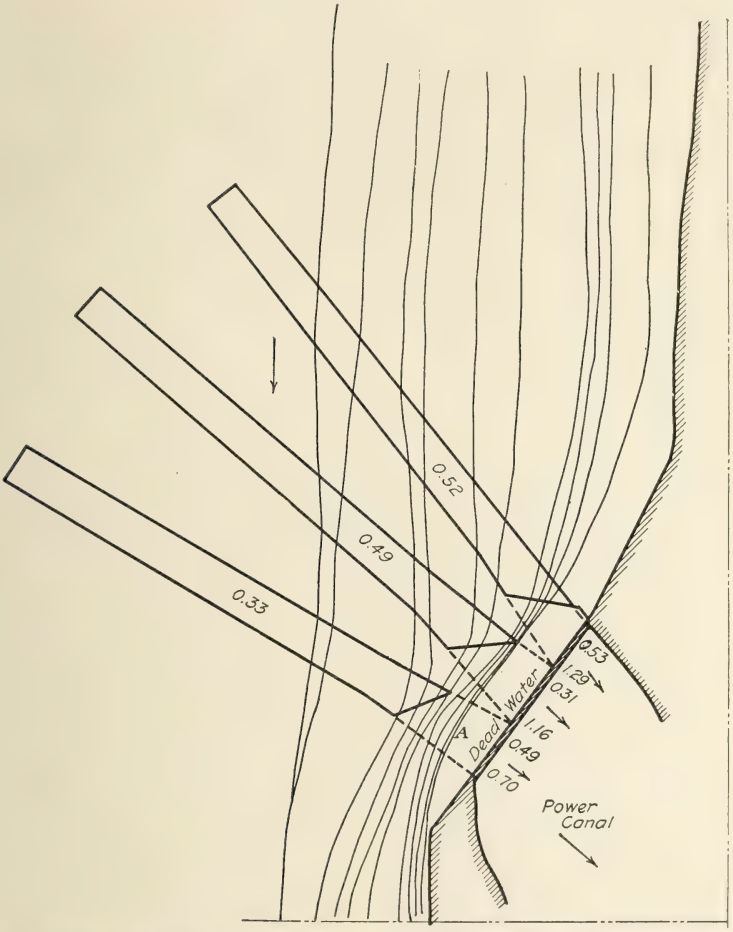


Fig. 10. Paths of Deep Floats with Intake *C* Drawing 8.1 Cu. Ft. per Sec.; River Gage, 560.5 Ft. Figures Give Velocities.

them entered the lower slot, the reason being that the amount of water taken out by each slot caused a decrease in the river velocity, which finally became critical and could not carry the floating matter past.

Triangular corners were next added, forming intake *C* shown in Fig. 10. A number of experiments were made with this arrangement with

different lengths of slots and different drafts, studies being made by current meter and floats. In this type floats 4.5 in. deep failed to go in, but the disadvantage was that a large eddy formed near the vertical curtain wall at *A*, which held the floats for some time but finally released them to go down the river.

That this intake drew water largely from near shore was proved when the slots were shortened without producing any material effects on the intake. The current meter invariably showed that where the water passed from the intake into the canal the velocity at the downstream side of the slot was very much more than at the upstream side, a feature that was undesirable and unexpected.

Some curves to show the effect of the intakes on the distribution of

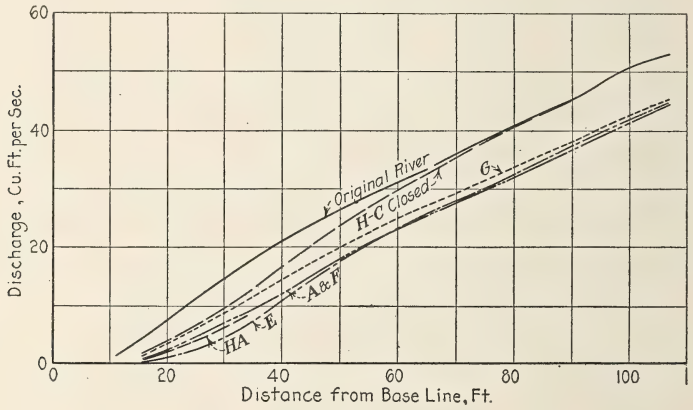


Fig. 11. Total Discharge Down the River at the Distances from the Base Line. Discharge Measured at the Bridge below the Intakes. The Letters on the Curves Denote the Intake Referred to.

water in the river are given in Fig. 11, where the upper one corresponds to the undisturbed river and the others to the intakes, none of which has much effect on the river beyond its own length, the two lines remaining a constant distance apart beyond the end of the intake.

The next type, *D*, consisted of a trench having a uniform width of 6.8 ft. and length of 18.8 ft., the depth below the river bed averaging about 1 ft. This trench was divided into three slots by vertical planks as shown in Fig. 12, the depth of the river being decreased on passing down over the intake for reasons already stated. With this intake left entirely open many floats went in, as the discharge velocity into the

canal was quite high, but inasmuch as the loss of head due to this high velocity could largely be recovered with a proper diffuser, it was thought worthy of trial. In the earlier trials with this type the lower slot proved to be of little value, but by raising the river bed below this slot it was made to take its full load.

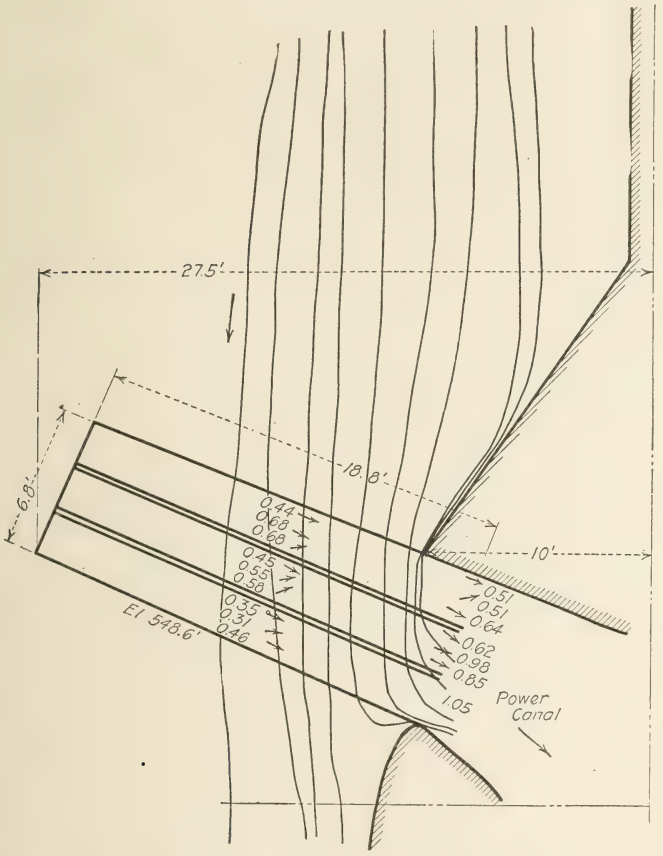


Fig. 12. Intake *D* Drawing 8.0 Cu. Ft. per Sec.; River Gage, 560.4 Ft. Paths of Deep Floats. Figures Denote Velocities in Slots.

The open form of this intake having proved ineffective, a vertical submerged wall was next used, and afterward a combination with this of a horizontal table 20 in. wide and with various positions of the diverter, but very little difference appeared to exist between this and the first type, and neither could be considered a solution to the problem. Triangular covers were also added, but the large eddy still remained and

it held the floats close to the intake and passed them back over it, although few of them entered. Different forms of diverters were tried for the purpose of reducing this sweep, and one scheme, intake *E*, is shown in Fig. 13 where the draft is fairly evenly distributed on the three tubes.

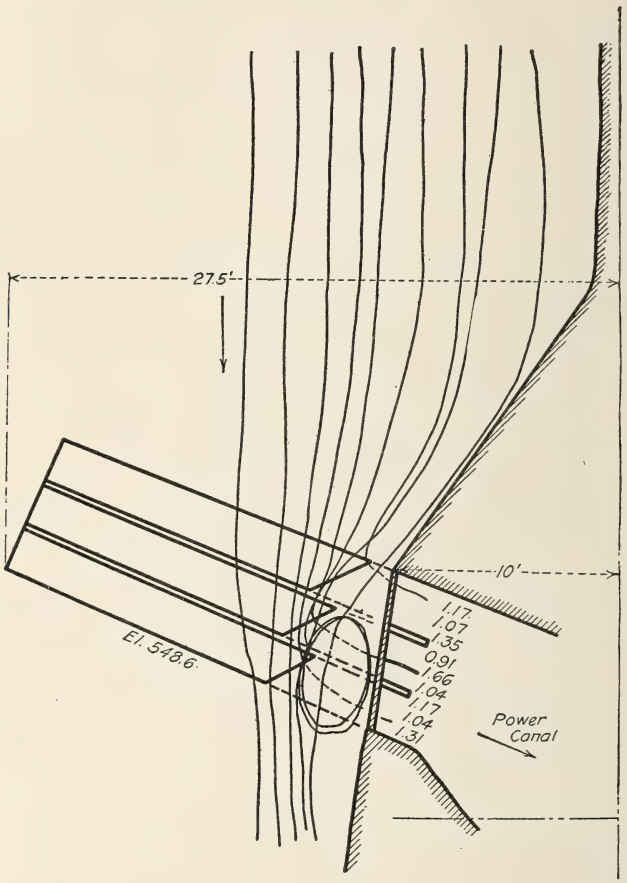


Fig. 13. Paths of Deep Floats with Intake *E* Drawing 7.72 Cu. Ft. per Sec. River Gage, 560.3 ft. Figures Denote Velocities in Slots.

This finished the work on the open intakes, none of which gave promise of meeting the conditions demanded. They did, however, suggest certain lines along which the later experiments were made.

CLOSED AND COMBINED INTAKE MODELS

The first of these was made from the open intake just described by covering over the slots with boards level with the river bed and leaving one opening 3 ft. by 1.94 ft. in each, in the position shown in Fig. 14. This design showed a marked improvement over those already tried in every respect except that there was an increased loss of head, but the

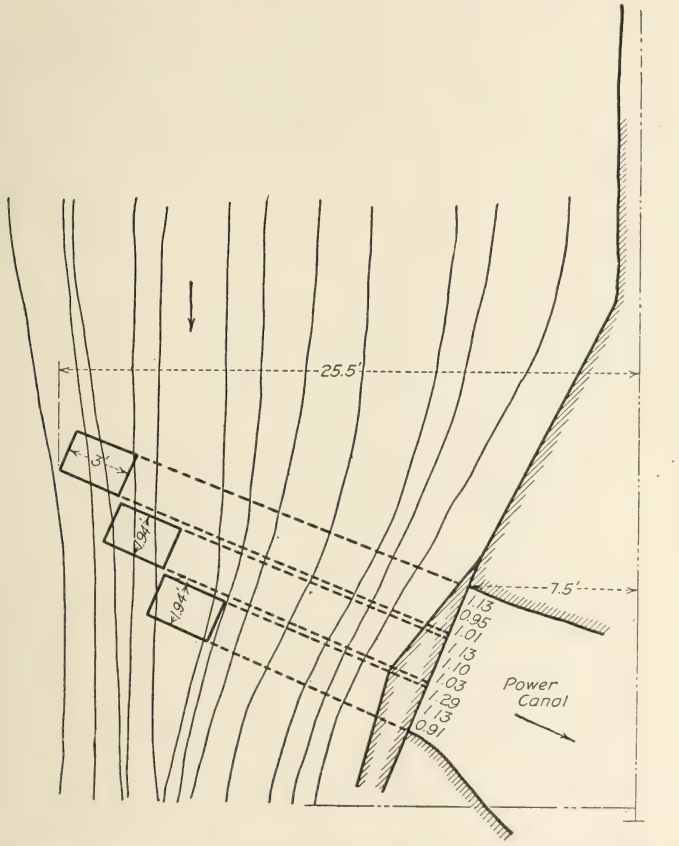


Fig. 14. Paths of Deep Floats with Intake *F* Drawing 8.1 Cu. Ft. per Sec. River Gage, 560.5 Ft. Figures Denote Velocities.

paths of the floats shown in Fig. 14 and effect of the draft shown in Fig. 11 indicate a fairly good type of intake. The current meter also showed very good distribution of the load over the various slots. Two features were evident: (*a*) there was a large friction loss, and (*b*) there was a marked tendency to draw water from a distance further

out than the intake tubes extended. The velocity was also lowered in the river below the intake.

Slots were next cut in the covers along the tops of the channels, these being narrowed down as they approached the shore for the purpose of distributing the draft along the length and to make the intake more effective over the entire area occupied by it. The results of this modification proved very encouraging, the friction loss decreased, and

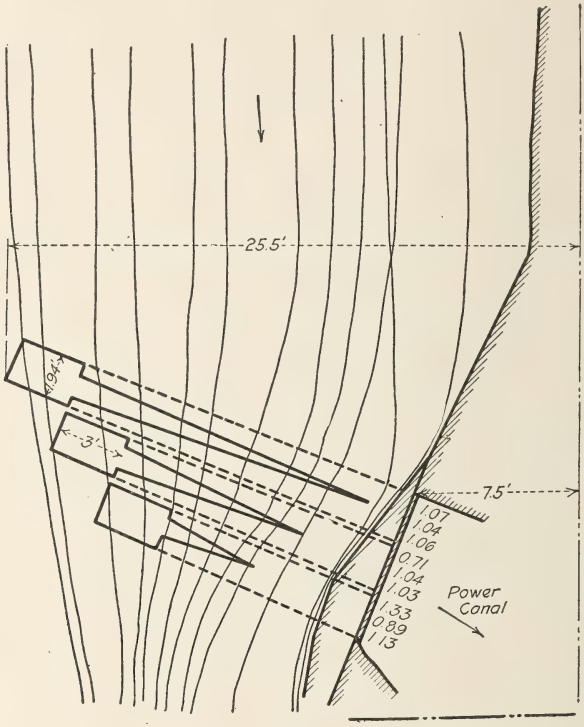


Fig. 15. Intake *G* Drawing 8.2 Cu. Ft. per Sec. with River Gage, 560.1 Ft. Figures Denote Velocities.

the stream lines were straighter than on any other of the models. Practically none of the floats entered the intake, not even those 3 in. deep and exposed to an upstream wind of 10 miles an hour. This type of intake formed the basis on which one of the second season's plans was based, but lateness of the season prevented a full investigation being made at this juncture. This intake is shown in Fig. 15 and the results obtained in Fig. 11.

During the first season two other forms of intake were suggested

and it was thought well to try them in a general way. From the original opening 6.8 ft. wide used in the last set of experiments the two intermediate planks were removed and replaced by a single one in the center, thus making two channels 3.3 ft. wide and lengthened to 25.75 ft. Each channel was then covered over in such a way that water could enter along the entire length of one side of each channel, the other side being closed: that is, the cover was nailed down solid to one edge of the channel and the other edge of the cover raised 0.30 ft. to let water in. There were thus two vertical openings 0.30 ft. high and 24 ft. long through which all the water entering the canal had to pass on its way

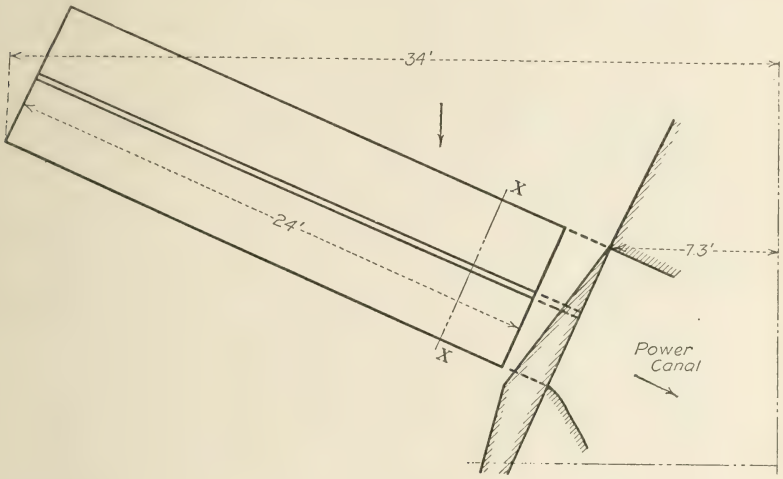


Fig. 16. Intake *H*.

through the closed tubes 1.75 ft. long to the power canal. (See Fig. 16.)

Various arrangements were tried with this by putting both slots upstream, Scheme *A*, Fig. 17, and one up and one down, Scheme *B*, Fig. 17, but, as one would probably expect, the intake was not a success, the floats entering the shore end of both openings, and the lower opening seemed to catch a large proportion of what came near it. Part of the trouble was undoubtedly due to the small depth of water on top of the cover, and possibly with more time for experiment a satisfactory device could have been made. There are, however, inherent defects, as uniformity of draft is impossible with constant width of opening in this type of intake, and also the change of depth that occurs at the intake due to the covers' forming a type of obstruction which pushed out the water, as a study of Fig. 11 shows. This means a marked decrease in

the water available at the intake and a very decided deadening of the water below it, causing ice to jam, as was indicated by the floats. There was also a standing wave above the opening.

A modification of this intake was next built by making the cover out of separate slats, somewhat in the form of a louver, and laid flush with the river bottom in the manner shown in Scheme *C*, Fig. 17. This type would evidently be troublesome and costly in construction and therefore objectionable from that standpoint, but when the slats were so adjusted that the openings for the water varied from nothing at the shore end to a desired amount at the outer end, the result was very good. Uniform width of opening for the entire length caused relatively heavy draft at the shore end and a bad eddy below it.

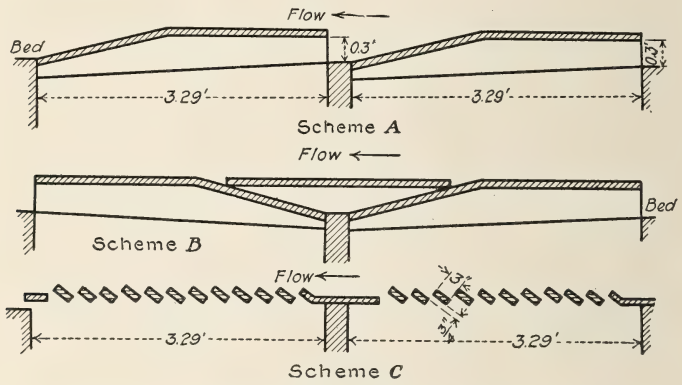


Fig. 17. Sections Through Intake Shown in Fig. 16 along Line *X-X*.

RESULTS OF EXPERIMENTS

When the experiments above described were completed, construction work on the new pipe line for the Ontario Power Company compelled the work to be discontinued, and this gave time for a careful study of the results. The work covered a careful investigation of a number of proposed intakes and further enabled certain conclusions to be drawn as to the desirable and undesirable features. These may be briefly summarized as follows, it being remembered that part of these conclusions apply only to a location similar to the one proposed:

a It appears that an open type of intake, *i.e.*, one where there is no physical structure to cut off the surface water, is not desirable. Such an intake failed to keep out surface debris, more especially when there was an unfavorable wind. Its losses are very small and cost of construction comparatively low.

b A vertical curtain wall extending well above and below the water surface, forming submerged openings for water, is of little value, as debris is drawn down its surface and into the intake. Making the wall wide at the bottom, so as to produce the effect of a tube instead of an orifice, improves the conditions.

c Draft of the water must extend over a considerable area, as any localizing of the draft produces excessive velocities and causes the entry of debris. There is also a stagnant area just below this point, in which an eddy forms, holding suspended material and passing it back over the intake.

d Unusual care is required to prevent localized draft. For long tubes with uniform openings along their length there is a drop in

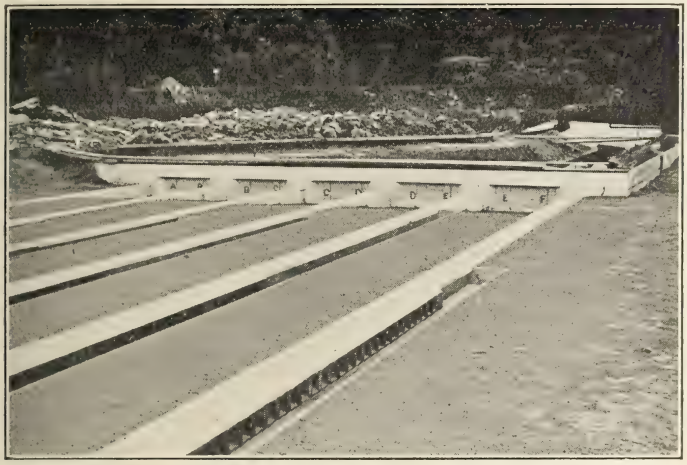


Fig. 18. View of Johnson and Wahlman Model, Taken from Bed of the Niagara River Just Below the Model. Welland River and Power Canal on the Right.

gradient inside the tube toward the power canal, and this causes concentration of draft at the inner end of such tubes, making the outer end of little value and causing high velocities at the shore end.

e The maximum velocity of water entering the intake must be low at all points.

The experiments indicated that at least two methods, after intakes *F* and *G*, might be used to meet the desired conditions, and consequently two forms of intake were devised, and the second season's work was done on these two only. The first of these intakes was designed by Messrs. R. D. Johnson and P. Wahlman, and consisted of a series of six tubes drawing in water for the greater part of their length; while

the second intake was designed by the author, and consisted of six large openings on the bed of the river, each connected with the power canal by a separate tube.

THE JOHNSON INTAKE MODEL

The Johnson intake model was made up of six parallel tubes, each

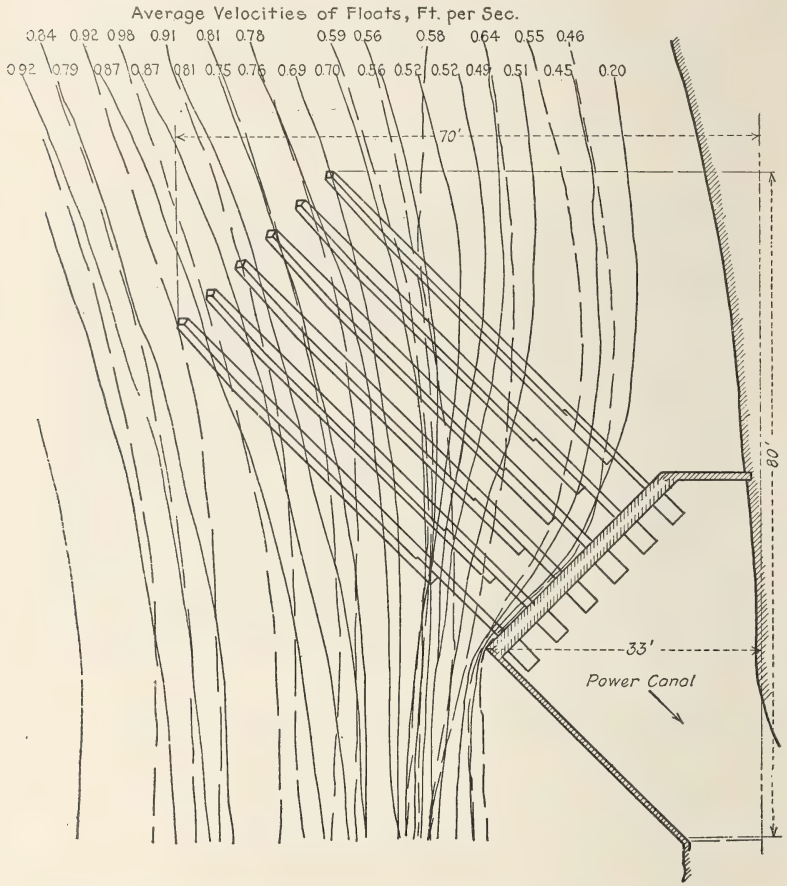


Fig. 19. Johnson and Wahlman Intake Model—Paths of Deep Floats. Broken Lines Correspond to Intake Closed and Drawing No Water. Full Lines to a Draft of 8.72 Cu. Ft. per Sec.; River Gage, 559.8 Ft.

having a total length of 69 ft. 6 in. and being placed at 5 ft. centers. Of the total length of the tube, the inner 4 ft. 6 in. served as a diffuser with expanding section; the next 55 ft. was of uniform size 10 in. square inside, while the outer 10 ft. tapered from the 10-in. by 10-in.

section to a 3-in-square section at the outer end. Along the face of the outer 40 ft. of each tube there was a vertical opening in which guide vanes were set so as to form ports which would direct the water inward along the tube axis. These are shown in place in Fig. 18.

The tubes had been carefully worked out theoretically and designed with sufficient shock loss to try to produce uniform draft along the entire outer 40 ft. Naturally the port areas have a relatively smaller area at the inner end than at the outer, and the areas and angles of the ports were very carefully graded to suit the desired conditions. The object of the design was to draw uniformly over an area 40 ft. by 25 ft. at the river bed, or in the full-sized intake over an area of 400,000 sq. ft., and hence the vertical component of the velocity would be very small.

A general view of this intake in position is shown on Fig. 19, together with the stream lines for a draft of 8.72 cu. ft. per sec., corresponding to 15,600 cu. ft. per sec. in the actual intake, with the river at El. 559.8 ft. For reference the stream lines with the intake closed are shown dotted, and it is seen that the draft is very uniform over the area.

TABLE 1 PITOT MEASUREMENTS IN TUBES

	Discharge in Tube—Cu. Ft. per Sec.				
Tube	One-quarter way in	Half-way in	Three-quarters in	Full discharge of tube	Measurement by weir
A	0.27	0.73	0.88	1.12	.....
B	0.26	0.70	0.76	1.18	.....
C	0.33	0.64	1.05	1.23	.....
F	0.31	0.68	0.94	1.24	.....
A	0.70	1.26	1.85	2.36	.....
C	0.74	1.20	1.73	2.48	.....
A	.....	.....	.....	2.11	
B	.....	.....	.....	2.10	
C	.....	.....	.....	2.09	
D	.....	.....	.....	2.14	12.90
E	.....	.....	.....	2.15	
F	.....	.....	.....	2.10	
			Total	12.69	

Pitot-tube studies were also made on this intake to find how effectively each section of the tube operated, and measurement of the discharge

was made for each quarter of the length of the part of the tube containing the ports.

These measurements showed a very uniform division of the discharge among the several tubes, the discharge for any one tube not differing more than a small percentage from the average for the six, and it was also interesting to find that the sum of the discharges measured by pitot-tube was within two to five per cent. of that taken by weir measurement at the lower end of the canal. In view of the fact that the velocities were usually between one and two feet per second and that the observations had to be taken with moderate speed in the field, these results are fairly satisfactory.

The distribution of draft in the tubes is shown in Table 1, which gives the discharges taken from an average of six velocity measurements at each section.

The loss of head in this intake was measured carefully and amounted to 1.45 in. with a draft of 15,000 cu. ft. per sec. (8.72 cu. ft. per sec. on the model) and was 2.15 in. with a draft of 20,000 cu. ft. per sec. In the first model the diffuser at the inner end was not well proportioned and a second set of experiments was made with an improved diffuser and also with the inner end of the tube shortened 10 ft. so as to bring the inner port 10 ft. closer to the shore. This modified intake, shown in Fig. 19, worked quite as well as the former one, indicating that the tubes could be reduced by 200 ft. in length, making them extend 1100 ft. beyond the diverter, without impairing their efficiency, and that possibly still greater reduction might be made.

The modified intake showed a reduction in friction loss of head to 0.70 in. at a draft of 15,000 cu. ft. per sec. and 1.20 in. at 20,000 cu. ft. per sec., which are only about one-half the former results. Lack of time prevented farther experimenting on this intake.

THE AUTHOR'S INTAKE MODEL

This intake was designed on a different line from the former one and its general appearance is shown in Figs. 20 and 21. There were six tubes with a diffuser on the inner end of each, and the outer end was a large rectangular opening 24 in. by 36 in.; the tubes were sunk below the bed of the river, with the opening lying on the river bed. The tubes all had a uniform depth of 10 in. and a width proportioned to produce uniform draft in each tube as well as possible. An examination of Figs. 19 and 21 gives the relative sizes of this and the former intake, and it is also evident that this intake draws from a narrow strip

of river reaching out diagonally from shore, rather than from the large rectangular area used by the Johnson scheme.

Fig. 20. The Author's Model, Taken from the Bed of the Niagara River Just Above the Intake (Grading Unfinished). Power Canal at Upper Centre, Metering Bridge on Right.

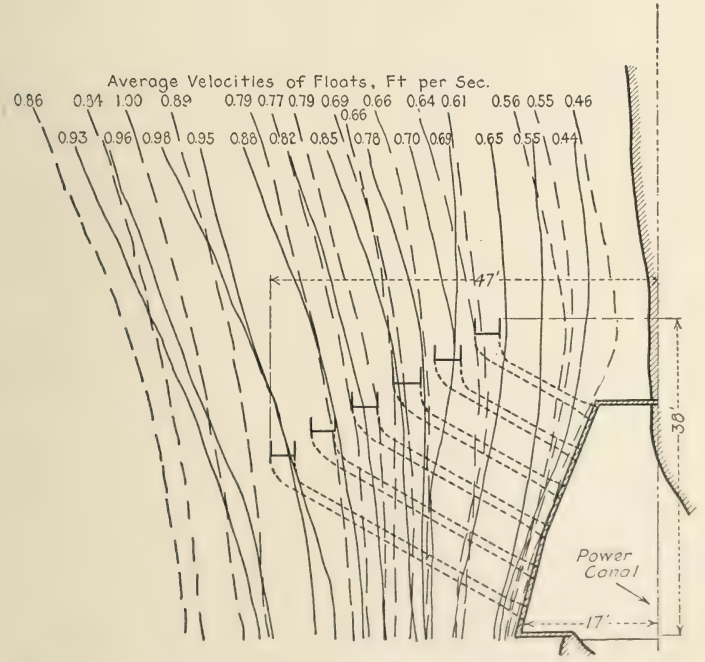


Fig. 21. The Author's Intake Model—Deep Floats. Broken Lines Show Paths of Floats with the Intake Closed and Drawing No Water. Full Lines are for a Draft of 9.56 Cu. Ft. per Sec.; River Gage, 559.6 Ft.

The results of float experiments on this intake at River El. 559.6 ft. when drawing 9.56 cu. ft. per sec., corresponding to 17,100 cu. ft. per sec. on the full-sized intake, are shown in Fig. 21, and the conditions in the river with the intake shut off are shown by broken lines, from which it will be seen that there would be a slight tendency for thickening of ice over the openings. The floats were 6 in. deep in many cases and no float entered the intake even at reduced river flow. Floats passing over the intake showed a slight hesitation on passing the downstream edge of the opening, but by comparing the mean velocities of two floats, one of which passed over the opening and the other passed between two openings, no difference was observable.

Pitot-tube studies on this intake were also made, and the results of some of them are given in Table 2; they show that the draft was quite evenly divided, and that slightly different proportions of tubes would make this more uniform still. The loss of head with a draft of 9.56 cu. ft. per sec. on the model was 0.59 in. and at 11.95 cu. ft. per sec. was 0.964 in., the former corresponding to the full-sized discharge of 17,100 cu. ft. per sec. and the latter to a discharge of 21,400 cu. ft. per sec., and the loss computed to the discharge of 15,000 cu. ft. per sec. is 0.46 in. in the first case and 0.47 in. in the second.

TABLE 2. PITOT-TUBE MEASUREMENT IN TUBES—DISCHARGE IN CU. FT. PER SEC.

Tube						
A	*B*	*C*	*D*	*E*	*F*	Total
1.69	1.64	1.63	1.59	1.53	1.57	9.65 (Weir gave 9.56)
2.08	2.02	2.09	1.95	1.89	1.96	11.99 (Weir gave 11.95)

It will be noticed that there is very good agreement between the weir and the pitot-tube measurements and similar agreement was found in all the experiments.

Both the Johnson and Wahlman intake and the author's intake were tried with reduced river discharges and also with drafts much in excess of the 15,000 cu. ft. per sec., as the above results indicate. Neither scheme was satisfactory if over 50 per cent. of the river flow was cut off, even when drawing its normal amount of water.

Figures 22 and 23 show that there is a marked similarity in the general effect of these two intakes as far as the river flow is concerned, and that both intakes affected the entire width of the river, as is evidenced by the fact that the two lines on each figure continually

diverge as they go out from shore. In this connection it will be well to reëxamine Fig. 11, in which only intake *G* had a similar tendency, the others having very little effect on the river beyond the point of the intake, being, no doubt, too small.

That the intakes must be made to draw from lines normal to the

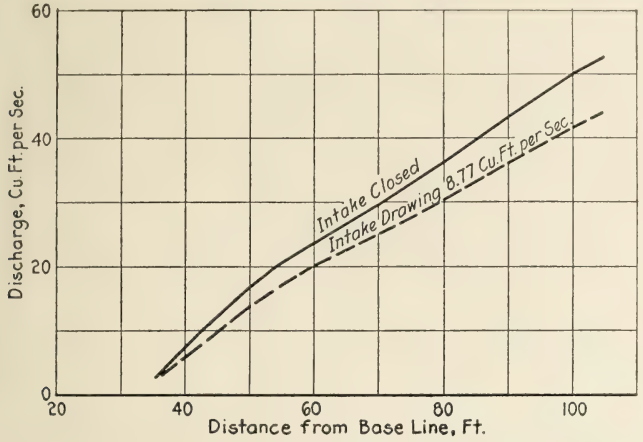


Fig. 22. Total Discharge Under Bridge with Johnson and Wahlman Intake.

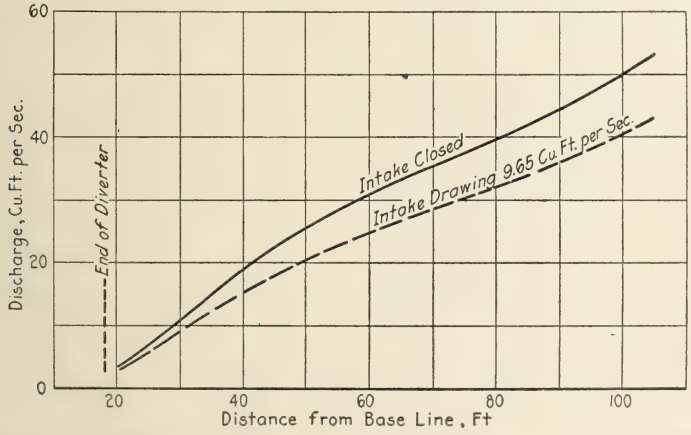


Fig. 23. Total Discharge Under Bridge with the Author's Intake.

shore rather than parallel with it is evident, and an effective design may be made to distribute its suction over a much greater distance than it extends.

Only a part of the experimental work done is shown in the paper owing to lack of space. The author expresses his thanks to the Hydro-Electric Power Commission of Ontario, Canada, for permission to publish these results.

PRODUCER GAS FOR ROAD TRACTION

By E. A. Allcut, *Associate Professor of Mechanical Engineering*

Introduction

With the continued and increasing consumption of gasoline for road vehicles, and the development of high-powered aircraft engines requiring large quantities of light fuel, it is evident that, in the near future, some alternative method of driving high speed light-weight engines must be devised. Much experimental work has been and is being done with the object of adapting heavy oil engines for this purpose, and while some measure of success has been achieved with large powers, the engine is generally too complicated, heavy and costly for the small powers used in road traction. When the suction gas producer reached a reasonable state of reliability and became widely used in combination with stationary gas engines, several portable types were designed and used for various purposes,[1] but in most cases these were too heavy and bulky for transport purposes, and moreover required large quantities of water for cooling and cleaning the gas before entering the engine.

In marine and motor boat work, where the conditions were not so exacting, some fairly satisfactory suction plants using anthracite, charcoal or coke were made, and during the war the increasing scarcity and high cost of gasoline in England and Europe led to the design and construction by Col. D. J. Smith of a small suction gas plant, which was mounted on a motor truck. This is claimed to have given satisfactory results, and the design was developed and improved after the war, when the author had the opportunity of inspecting and testing a "Smith" producer which was connected up to a stationary four-cylinder gasoline engine ($3\frac{3}{4}'' \times 5''$) coupled to a Froude dynamometer, and upon this plant a considerable amount of experimental work was done during the spring of 1920.

Observations were also made under running conditions on a 3-ton motor truck, a Ford car, and a motor boat equipped with this type of power generator.

A further development along similar lines (the "Parker" producer)

[1] See Robson, "Power Gas Producers," (1908), p. 125. Also Rambush, "Modern Gas Producers," p. 338.

was tested on the road in the fall of 1920, and although encouraging results were obtained on both designs, they were not sufficiently conclusive and reliable to justify the application of this type of generator on a commercial scale. It was considered, however, that the difficulties experienced would ultimately be overcome by improved designs and that the ultimate success of the gas producer in this connection was a matter of time and experience.

Since that time further developments have taken place, and Messrs. Thornycroft of Basingstoke, England, have put on the market a standard truck in which a suction gas producer is incorporated.[2] The Hungarian State Railway has developed a similar plant,[3] and several automobile firms in France, Germany and Central European countries have also adopted the gas producer system. Several of these systems have been described in the press[4] during the past few years, but although slightly different in detail, they are all similar in principle.

It should be recognized from the outset that this system is unlikely to be suitable for passenger cars, but its main field of application will probably be in truck and traction work, where the conditions of working and the care and attention available are much more conducive to its successful operation.

PRACTICAL DESIGNS AND TEST RESULTS

The size of gas producer employed for traction work is much smaller than that generally used for stationary plants. The firebrick or corundum lining usually has an inside diameter of from 10 to 12 inches, and the overall size of the producer is generally about 14 to 18 inches diameter (or square) and 2½ to 4 feet high, varying with different designs. Some producers have shaking grates and mechanical fuel feed, but for traction purposes it is advisable to have as few moving parts as possible. In some cases wet scrubbers are used for cleaning and cooling the gas, but although these are generally more effective than dry scrubbers both for cleaning and cooling, their cost, complication, and the extra cooling water required are decided disadvantages, and therefore an air cooled scrubber is preferable.

The advantage of the suction over the pressure system of gas generation is that there is no leakage of poisonous gas into the atmosphere, all leakage being that of air into the plant. Such leakage, of course, dilutes the gas and therefore all joints should be made and kept tight.

Ample arrangements must be made for the separation and collection of

[2]Times (London) Trade Supplement, Sept. 2nd, 1922.

[3]Automobile Engineer, May, 1923.

[4]*Cf.* "Mail and Empire," Toronto, Jan. 23, 1924.

dust and moisture from the gas, as considerable difficulty was experienced in the earlier installations with moisture collecting on the sparking points when starting up, and also with fouling of plugs, valves, and lubricating oil in actual running.

Usually no great difficulty is experienced in starting up from cold, but during this operation the fire is generally blown up by a hand-propelled fan, and arrangements must be made to exhaust the gas generated during this operation, on account of the CO and CO_2 present in the gas.

A great disadvantage of the suction system is its comparative inflexibility. Under constant load and speed a suction plant runs very well, but when the engine is slowed up or stopped, the fire cools down and the gas subsequently supplied is of poor quality. This is particularly objectionable in traffic or hilly country. Messrs. Thornycroft supply an exhauster to keep the fire in condition and in other cases the clutch is allowed to slip when running slowly in traffic. This keeps the engine running at a high speed and enables it to pick up better when the load comes on again. In this connection it is important that the water or steam supplied to the producer shall be adjusted automatically to maintain a constant ratio of air to water supply, as otherwise an excess of steam will be obtained at light loads or slow speeds, thus further cooling down the fuel bed and producing poor gas.

The fuels generally employed are anthracite, coke and charcoal, all of which are usually satisfactory, but the power given out by an ordinary gasoline engine running on suction gas is about 20 per cent. less than that obtained from liquid fuel. For commercial applications, therefore, it will either be necessary to increase cylinder dimensions, or to reduce the rated load of the truck. One difficulty frequently met with in gas producer work is the formation of clinker which obstructs the flow of air through the fuel, produces poor gas and finally stops the plant. Non-clinkering fuels should therefore be used and arrangements made to clean and consolidate the fire during running. In some cases the shaking of the vehicle may do this, but much depends upon the design of the producer, the method of feeding the fuel and the nature of the fuel used.

It may be pointed out that generally the fire hazard is less with solid than with liquid fuels, and that as there is no danger of "pinking" or detonation, higher compressions may be employed with safety, but in the latter case, although the efficiency may be increased, starting will be more difficult.

The fuel consumptions generally given are for running tests over measured distances, but it should be noted that the fuel consumption continues (to a much less extent) when the truck is stopped. Con-

sumption over measured distances, therefore, do not form true comparisons between gasoline and gas producer trucks, but as in most instances these are the only figures available, they will be used to give some idea of the fuel economy of these vehicles under running conditions.

No description will be given of the details of these plants as they are adequately described and illustrated in the articles enumerated in the footnotes.

"Parker" Plant[5]

Guaranteed consumption of foundry coke for 3-ton truck fully loaded is 3 lbs. per mile over 100-mile run. Gasoline consumption of same truck is 0.17 Imperial gallons per mile.

The water used for gas making in all these plants is about half the weight of fuel consumed.[6]

"Smith" Plant[7]

Col. Smith gives the following comparison in fuel consumption:

	5-ton steam truck	5-ton gasoline truck	5-ton producer gas truck
Gross load tons	12	9	9.5
Lbs. fuel per mile	14	1.33	1.56
Lbs. fuel per *nett* ton per mile	2.8	.26	.312

When the difference in cost between gasoline and the various solid fuels is taken into account, it is evident that the cost of fuel for running a producer gas truck is very low.

Thornycroft Plant

Road tests taken over a 28-mile run at 12-13 miles per hour on a 4-ton truck:

Anthracite.....lbs. per mile 2.51 Water used.....1.61 lbs. per mile
Charcoal..... " " " 2.9 " " .....1.25 " " "

The charcoal is produced in the works of Messrs. Thornycroft at Basingstoke (England) by running the exhaust gases from the gas

[5]See "Automotive Industries," Sept. 8-15, 1921, and "Engineering," June 17th, 1921.

[6]Proc. Inst. Mech. E., April 28th, 1911.

[7]See "Producer Gas for Motor Vehicles," D. J. Smith, Journal Inst. Aut. Eng., Jan. 8th, 1920. Also "Engineering," vol. 109, pp. 59 and 92, and "Automotive Industries," Sept. 8-15th, 1921.

engines in their power station, through an airtight steel box into which the waste wood or other substances to be carbonized are placed.

The analysis of gas obtained varies considerably with the type of plant, conditions of fire, water supply, etc., but Table 1 gives a number of analyses obtained under running conditions from "portable" gas producers.

TABLE 1

Load	Fuel	CO_2	O_2	CO	H_2	CH_4	N_2	Cal.[8] Value nett	Remarks
Stationary engine with brake	A	6.0	2.4	13.6	27.5	0.4	50.1	130	load 10 H.P.
	A	8.0	0	12.0	36.0	0	44.0	145	no load
	C	6.8	2.0	21.6	26.4	0	43.2	150	5 min. after starting engine
	C	6.8	6.0	9.2	29.0	0.4	48.6	119	25 min, after starting engine
	A	10.0	1.6	6.4	25.6	0.8	55.6	104	no load
	A	6.0	2.4	13.6	27.5	0.4	50.1	130	load 10 H.P.
4-ton truck on road	A	7.8	1.3	18.8	16.6	1.8	53.7	130	2-ton load—full throttle
		4.0	3.5	19.5	23.5	2.3	47.2	157	Gas temp. 760° C.
		1.6	0.5	29.5	15.5	4.6	48.3	190	" " 1150° C.

It will be seen from this table that the net calorific value of the gas varies from 104 to 190 B.T.U. per cu. ft. and averages about 130. This is suitable for internal combustion engines, but anything below 100 B.T.U. may be considered too poor for road traction.

TORONTO EXPERIMENTAL PLANT

This gas producer was designed for experimental work so that the effects of different variables on the quality of gas and efficiency of plant might be studied.

It consists (Fig. 1) of a cast iron shell and top cover, furnished with the ordinary fuel hopper valve and poking holes. This is supported on a

[8]The Nett Calorific values used for the various gases are average N.T.P. values—CO = 342, H_2 = 290, CH_4 = 955 B.T.U. per cubic foot. See Rambush, "Modern Gas Producers," p. 72.

NOTE.—A = Welsh Anthracite, C = Peat Charcoal.

Properties of Peat Charcoal used:

Moisture.....5.65% Volatiles....31.75%

Ash.....9.43% Sulphur..... .58% Total Carbon....64.87%

Cal. Value (B.T.U. per lb.) Gross 11463. Nett 11209.

mild steel ashpit provided with a dropping grate and a plate for supporting the firebrick linings. The latter consist of fireclay tubes each 19 inches outside diameter and respectively 15, 12, 10 and 8 inches inside

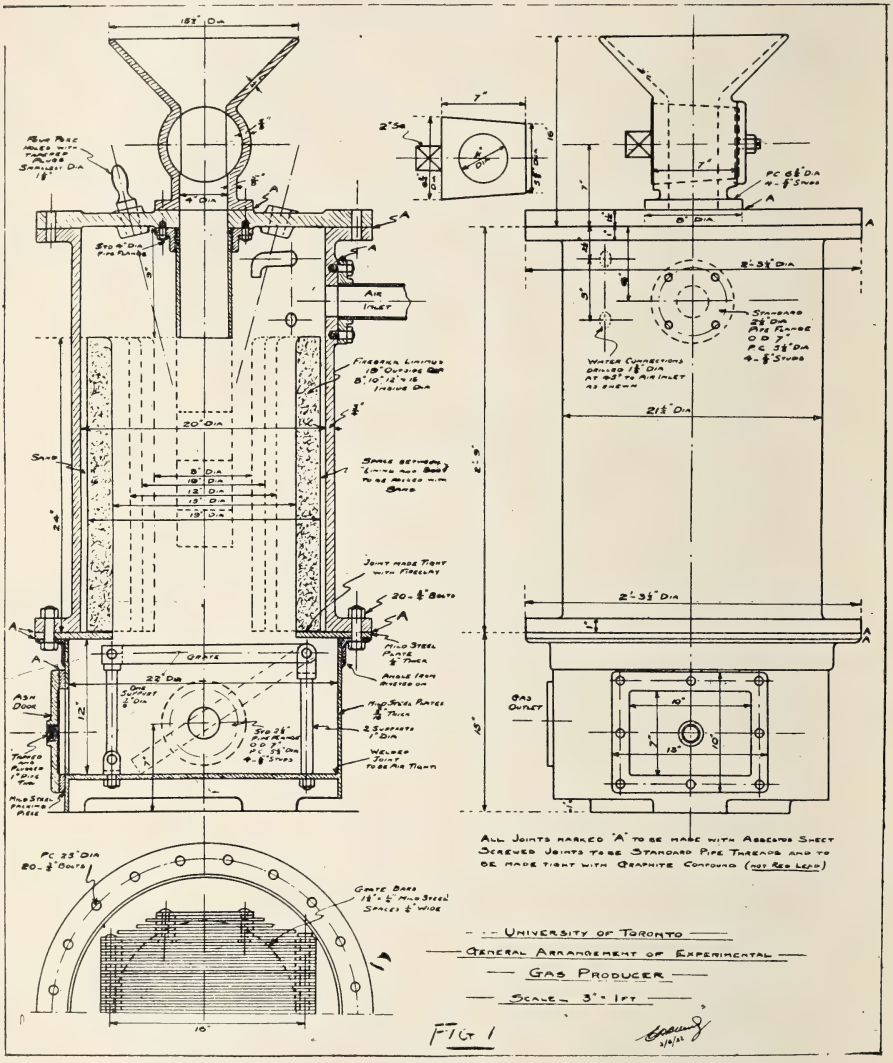


FIG. 1.

diameter. Tubes of different lengths may be screwed into the flange at the top to vary the depth of fuel bed by steps from 8 to 24 inches. The air is supplied through a measuring nozzle by a motor driven Roots blower and the piping is so arranged that air can be delivered to

the top or bottom of the producer at will, giving an up or down draft producer as required (Fig. 2).

The water supply is obtained from a tank suspended from a spring

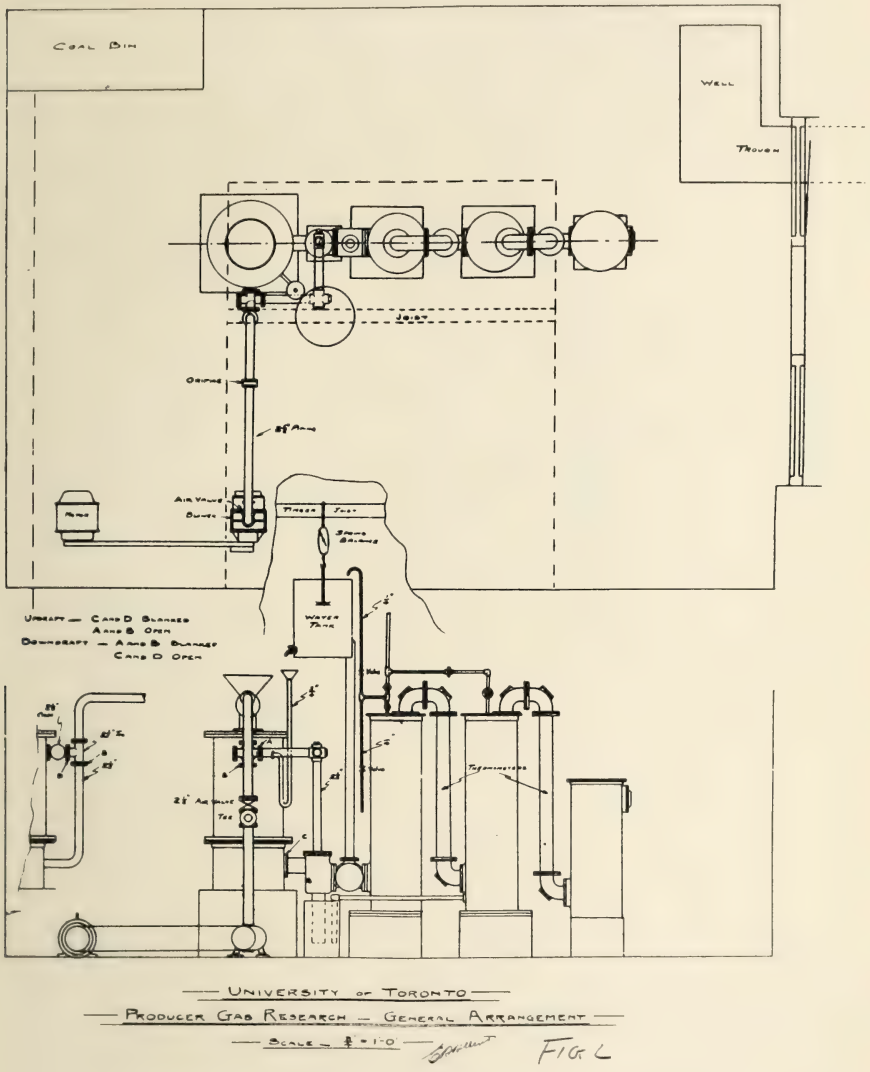


FIG. 2.

balance, and the temperature of gas leaving the producer is measured by means of a calibrated thermocouple.

With these arrangements the effect of the following variables may be investigated on producers of small size:

(*a*) Direction of draft (up or down).
(*b*) Nature of fuel.
(*c*) Diameter of fuel bed.
(*d*) Depth of fuel bed.
(*e*) Velocity of air supply.
(*f*) Ratio of air to water supply.

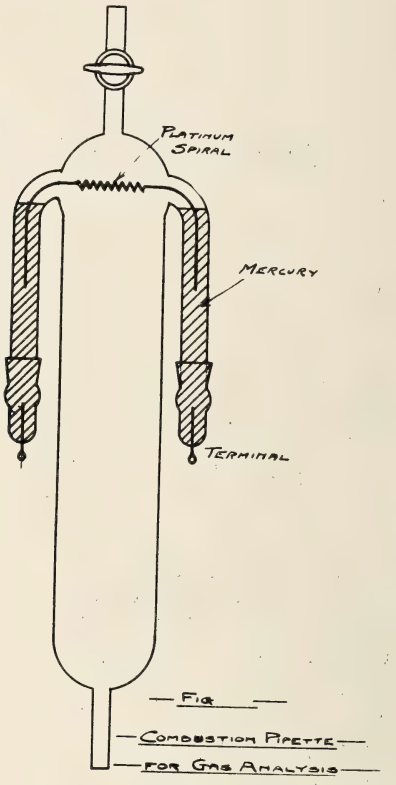


FIG. 3.

Samples of gas for analysis were taken from the pipe connecting the producer to the scrubber, and these samples were analysed in a gas analysis apparatus devised by the U.S. Bureau of Mines.[9]

On account of the use of water in the combustion pipette some trouble was experienced with the connections to the platinum spiral. The points where the copper leads were connected to the platinum frequently became hot, cracked the glass tubes in which the wires were sealed and caused leakage. Several other forms of pipette were tried

[9]See Bulletin No. 42 Bureau of Mines, "The Sampling and Examination of Mine Gases and Natural Gas," p. 43, Fig. 17.

and finally that shown in Fig. 3. was found to be satisfactory In this pipette no solid joint was used, but the copper leads were sealed into the glass arms, which were filled with mercury and the two ends of the platinum spiral also dipped into the mercury, thus giving good contact. The percentage of CO present in the gas was obtained by passing the gas (after absorbing CO_2, O_2 and heavy hydrocarbons) successively through old and new solutions of Cuprous Chloride. The "bubbling" pipettes provided for this absorption were very satisfactory and con-

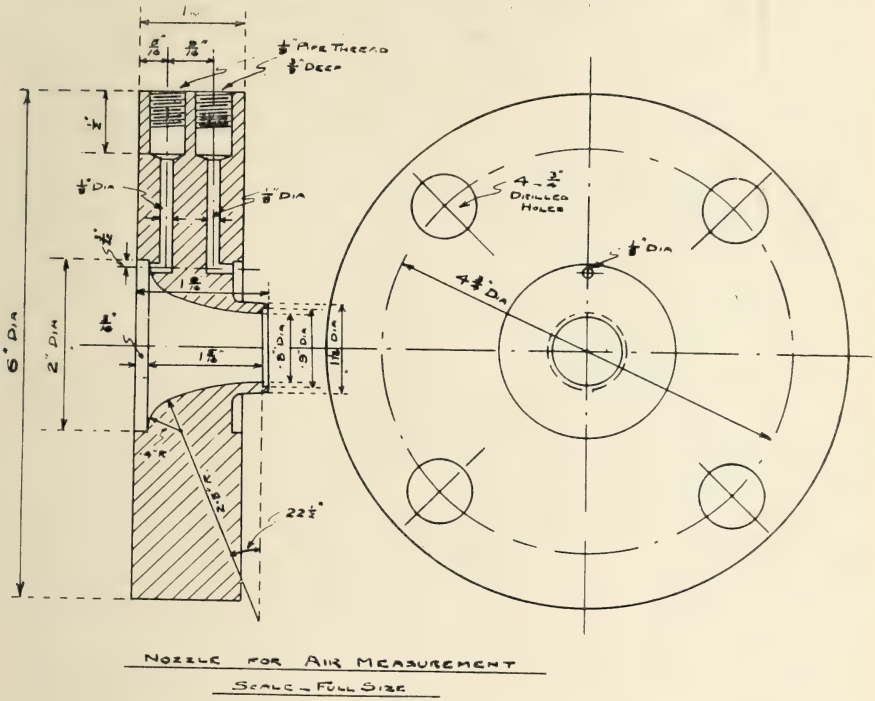


FIG. 4.

siderably reduced the time required as compared with ordinary pipettes.

The volume of air delivered per hour to the producer was calculated from the drop in pressure across the nozzle shown in Fig. 4. The contour of the nozzle conforms to the curve of the Verein Deutsche Ingenieure.[10]

An approximate delivery curve (Fig. 5) was worked out for experimental purposes, but the actual calculated values given in the tables were worked out from Reavell's formula in each case.

The gauge used for indicating the fall of presssure across the orifice was a direct lift gauge in which the position of the starting tube is ad-

[10]See Reavell on "Air Compressors," Inst. Mech. Eng., Nov. 24th, 1922.

justed by a vertical micrometer screw. This type of gauge has been previously described.[11] The alcohol used in the gauge had a specific gravity of .823 at 80° F.

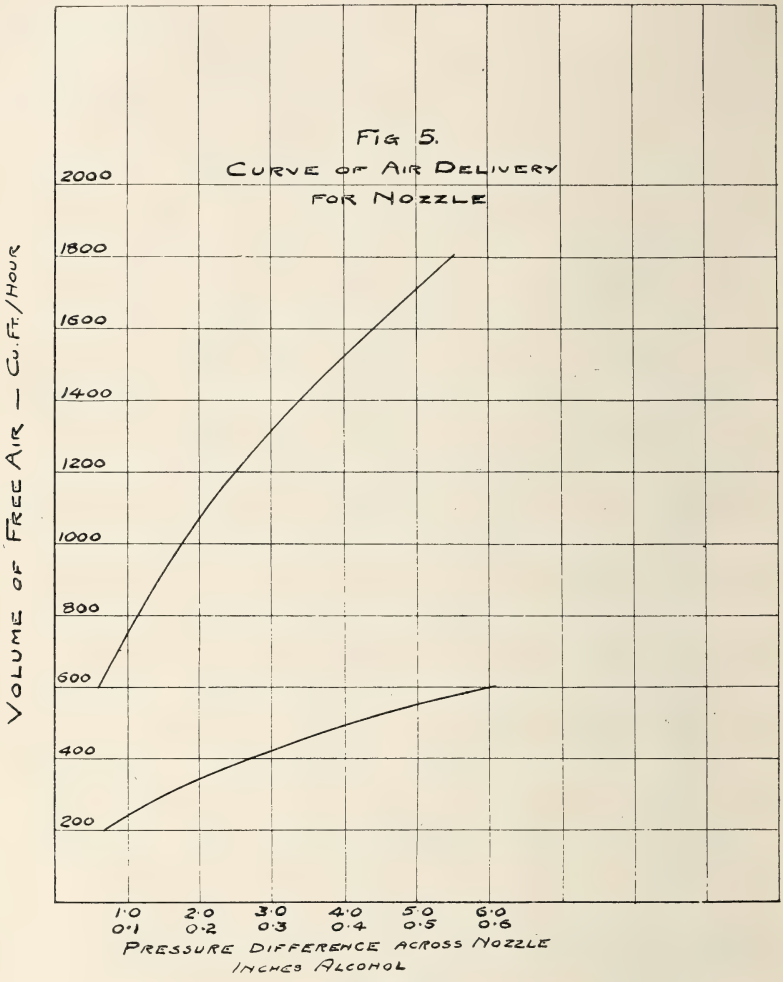


FIG. 5.

TEST RESULTS

The first series of experiments was undertaken to investigate the suitability of down draft producers for portable plants of small size. One of the chief difficulties in connection with the use of gas for power

[11]See University of Toronto Engineering Research Bulletin No. 2, pp. 50 and 58 (Fig. 13).

production is that of cleaning the gas and separating out the volatile matter before the engine cylinder is reached. With bituminous coals and other fuels rich in volatile matter this difficulty makes the use of such fuels impossible in a small plant, and therefore narrows considerably the field of choice as far as solid fuels are concerned. Anthracite is expensive and limited in distribution, and suitable coke cannot always be obtained, while bituminous fuels are widely distributed and may usually be obtained at reasonable prices. The down draft producer has been used in large sizes with a fair amount of success, and if it could be successfully adapted to small sizes, the problem would be simplified considerably.

An attempt to apply the down draft principle to a small gas producer is made in the "Stewart" plant,[12] but what measure of practical success has been obtained with this design is not known to the writer. In this instance a side chamber is used to distil off the volatile matter from the fuel and this volatile matter is then caused to pass through the hot bed of fuel in an ordinary up-draft producer. The down draft principle, therefore, is only partially employed in this case.

The experiments herein described were made on fuels containing little or no volatile matter, in order to eliminate complications as far as possible in the preliminary stages.

The quantity of water used during each test was obtained from the readings of a calibrated spring balance from which the water tank was suspended, but in addition to this, the quantity of water vapour entering the producer with the air was also calculated from the readings of a wet and dry bulb thermometer, and the total water feed was considered to be the sum of these two components plus the small quantity of water distilled from the fuel.

In all tests no readings were taken until the expiration of 1½ to 2 hours after lighting the fire, this time being allowed for conditions to become steady before each test started.

Tests Nos. 1 to 5 (Table 2) were made upon Anthracite I having the following characteristics:

Ash	16.6%
Volatile matter	17.9%
Calorific value	13,360 B.T.U. per lb.
Specific gravity	1.417
Weight per cubic foot coal as used	44.2 lbs.

The anthracite used for tests 6 to 13 was a new consignment intended to be of similar quality to that previously supplied, but actually it had a much greater ash content and its calorific value was lower than that of Anthracite I:

[12] "Automotive Industries," Sept. 15th, 1921.

Ash.....22.3%
Volatile matter..... 8.3%
Calorific value.....12,400 B.T.U. per lb.
Specific gravity..... 1.43
Weight per cubic foot as used.....43.5 lbs.

From these figures 1 cubic foot of solid anthracite weighs 88.5 lbs., and as the actual weight of coal present was 44 lbs., it follows that there were about 50% of voids present in the fuel bed, neglecting the space taken up by the ash in the lower parts of the furnace.

Tests 1 to 13 were made with different rates of air supply, and various ratios of water to air in order to ascertain the most favourable conditions for a 12-inch diameter furnace and the best quality of gas obtainable under these conditions.

Tests Nos. 14 and 15 were made on peat charcoal supplied by the Department of Mines, Ottawa. The weight of this was 24 lbs. per cu. ft., its calorific value, 11,720 B.T.U. per lb., and ash content 9.3%.

In all tests the fuel depth used was 24 inches.

TABLE 2.

Fuel	Anthracite No. I			
Test No	2	3	4	5
Fire lighted	9-10	9-15	9-5	9-10
Test started	11-30	10-45	11-0	11-0
Test stopped	4-30	3-45	4-0	4-0
Duration of test—hours	5.0	5.0	5.0	5.0
Barometric pressure—ins	29.71	29.82	29.71	29.74
Pressure of air entering producer—ins. water	5.0	3.4	2.6	7.22
Pressure drop in air nozzle—ins. alcohol	1.82	1.145	.586	2.72
Air temperature to nozzle °F.	84	88	86.5	92
Atmospheric air—dry bulb °F.	80	85.3	84.7	90
" " —wet bulb °F.	74	78.6	78.5	80.7
Humidity per cent	75	74	75.7	67
Air used per hour—cu. ft	1020	800	576	1242
Water in air per hour—lbs	1.11	1.07	.786	1.745
Water from tank per hour—lbs	7.0	5.70	4.45	8.40
Water from coal per hour—lbs	.55	.13	.065	.135
Total water to producer per hr.—lbs	8.66	6.90	5.30	10.28
Water used per lb. coal—lbs.[13]	1.095	1.025	1.07	1.22
Coal used per hour—lbs.[13]	7.9	6.725	4.95	8.43
Moisture in coal—per cent	7.0	2.0	1.3	1.6
Ash in coal—per cent	16.1	13.5	17.3	19.5
Gas Analysis: CO_2 per cent	9.9	9.3	10.4	11.7
(Average) O_2 "	1.0	1.1	.7	1.1
CO "	14.9	13.9	13.1	11.8
H_2 "	11.0	20.1	9.9	4.9
CH_4 "	.3	.5	.8	1.3
N_2 "	62.9	55.1	65.1	69.2
Higher Cal. Value—B.T.U./cu. ft	116	122	87	71.1
Lower Cal. Value—B.T.U./cu. ft	84.5	110	81	67.0

[13]Probably incorrect on account of accumulation of ash in fire.

TABLE 2—(*continued*)

Fuel	Anthracite No. 11					
Test No.	6	7	8	9	12	13
Fire lighted	9-5	9-30	9-10	9-15	9-15	9-20
Test started	11-0	11-15	11-0	11-30	11-5	11-0
Test stopped	4-0	4-15	4-0	4-0	3-35	4-0
Duration of test—hours	5.0	5.0	5.0	4.5	4.5	5.0
Barometric pressure—ins.	29.84	29.54	29.89	29.81	29.83	29.73
Pressure of air entering producer—ins. water	4.6	2.5	4.3	8.03	12.3	7.8
Pressure drop in air nozzle-ins. alcohol	1.38	.597	.954	1.26	1.116	1.67
Air temperature to nozzle—°F.	86	80.5	82	85	78	81
Atmospheric air—dry bulb—°F.	82	78.6	79	80	74.9	78.3
Atmospheric air—wet bulb—°F.	76	73.0	68.6	70.9	67.7	72.2
Humidity per cent	76	77	59	64	69	75
Air used per hour—cu. ft.	885	585	734	860	808	985
Water in air per hr.—lbs.	1.11	.666	.65	.857	.748	1.09
Water from tank per hr.—lbs.	5.10	4.00	5.00	6.29	8.15	12.6
Water from coal per hr.—lbs.	.07	.041	.013	.062	.066	.09
Total water to producer per hour—lbs.	6.28	4.707	5.663	7.209	8.964	13.78
Water used per lb. coal—lbs.[14]	.85	.81	.895	1.05	1.345	2.29
Coal used per hour—lbs.[14]	7.42	5.81	6.33	6.86	6.66	6.0
Moisture in coal—per cent.	0.9	0.7	0.2	0.9	1.0	1.5
Ash in coal—per cent	22.4	22.6	23.0	23.3	19.1	24.1
Gas Analysis: CO_2 per cent.	9.3	11.0	9.9	11.0	11.7	11.0
(Average) O_2 "	.9	1.0	.9	1.0	.9	1.0
CO "	13.2	11.2	14.7	13.8	8.7	12.8
H_2 "	6.8	8.3	7.3	7.9	8.5	7.1
CH_4 "	1.5	.4	.3	.3	.6	.5
N_2 "	68.3	68.1	66.9	66.0	69.6	67.6
Higher Cal. Value—B.T.U./cu. ft.	84.4	71.1	78.7	77.5	65.1	73.5
Lower Cal. Value—B.T.U./cu. ft.	79.1	66.2	74.4	72.9	60.1	69.2

[14]Probably incorrect on account of accumulation of ash in fire.

TABLE 2—(*continued*)

Fuel	Peat Charcoal		Anthracite No.
Test No	14	15	16
Fire lighted	9-20	9-5	9-30
Test started	11-0	10-30	11-0
Test stopped	2-0	12-33	3-0
Duration of test—hours	3.0	2.05	4.0
Barometric pressure—ins	29.88	29.77	29.9
Pressure of air entering producer—ins. water	7.8	9.4	7.5
Pressure drop in air nozzle—ins. alcohol	1.70	1.77	1.735
Air temperature to nozzle—°F	82.1	83.3	77.7
Atmospheric air—dry bulb—°F	77.5	77.2	74.5
Atmospheric air—wet bulb—°F	73.2	73.2	69.0
Humidity per cent	82	83	80
Air used per hour—cu. ft	987	1012	1000
Water in air per hour—lbs	1.165	1.19	1.05
Water from tank per hour—lbs	12.17	13.35	7.60
Water from coal per hour—lbs	.794	1.01	.13
Total water to producer per hour—lbs	14.13	15.55	8.78
Water used per lb. coal—lbs	.982	.846	.995
Coal used per hour—lbs	14.42	18.37	8.81
Moisture in coal—per cent	5.5	5.5	....
Ash in coal—per cent	9.7	9.1	....
Gas Analysis: CO_2 per cent	9.8	11.7	10.5
(Average) O_2 "	1.5	1.0	1.0
CO "	16.8	13.8	12.4
H_2 "	12.0	14.5	7.2
CH_4 "	1.9	1.9	1.4
N_2 "	58.0	57.1	67.5
Higher Cal. value—B.T.U./cu. ft	119.0	117.2	82.1
Lower Cal. value—B.T.U./cu. ft	110.4	107.4	76.7

[15]Probably incorrect on account of accumulation of ash in fire.

Considerable difficulty was experienced (particularly in the tests made on Anthracite No. II) with the accumulation of ash in the fire, which obstructed the passage of the air blast, and in the case of tests Nos. 10 and 11, this was so serious that the tests had to be stopped, on account of the limited capacity of the blower. For this reason no tests were made on Anthracite No. II with air supplies exceeding 1000 cu. ft. per hour. The increase of resistance with accumulation of ash was reflected in the indications of the air pressure gauge and in some cases readings as high as 14 inches of water were obtained. This resistance is important in all cases, but is particularly so when the air is drawn through the producer by the suction stroke of the engine. Although the fire was poked every hour, it was found difficult to get rid of the ash, and if fuels containing 20% or more of ash are used it is probable that a grateless producer, with some means of discharging ash continuously and automatically, must be employed.

The very poor quality of gas produced over a wide range of air and water feed is noteworthy. It is known[16] that down draft producers generate poorer gas than those of the up draft type. In the present series of experiments only one test with anthracite gave an average calorific value (lower) exceeding 100 B.T.U. per cubic foot, and when attempts were made to reproduce the conditions with Anthracite No. II (tests 6 and 9) very poor results were obtained.

The comparatively high calorific value obtained in test No. 3 was due to the abnormal percentage of hydrogen present in the gas.

In all tests one sample of gas was taken each hour midway between poking times, and the analyses given in the table are the average percentages of each constituent. In this test individual figures for hydrogen varied from 18.0 to 22.9% and there is no doubt that the average figure given in the table represents the actual composition of the gas produced. It is curious, however, that even when the amount of water supplied was greatly increased (tests 12 and 13) it was found impossible to approach this figure. Test No. 19 was made for the purpose of ascertaining whether the distribution of water in the producer had any effect on the results obtained. For this test the water spray was placed in the air pipe in such a way as to get the maximum atomizing effect instead of being fed directly to the producer. This change produced no improvement.

The percentage of CO present in the gas is also low in all tests, and as in the case of hydrogen, does not appear to be greatly affected by changes in the rate of air or water supply over fairly wide ranges. The range of these experiments may be extended by using the smaller pro-

[16]See Rambush, "Modern Gas Producers," p. 314.

ducer linings, which will allow higher air velocities to be used with the same blower.

Experiments Nos. 14 and 15 show that peat charcoal is very suitable for this class of work, in fact much more so than the anthracite used. The tests were of short duration in these cases because of the small quantity of charcoal available. Even in this case, however, the quality of gas was not so high as that from an updraft producer working under similar conditions, and in view of the small percentage of volatiles in peat charcoal the peculiar advantages of downdraft producers do not apply to this fuel.

Unless a considerably better quality of gas can be obtained from bituminous fuels (and this is improbable), the results of these experiments indicate that the downdraft producer is unsuitable for traction work on account of

(*a*) the difficulty of keeping the fire clean,

(*b*) the large increase of resistance to the passage of air after running for a few hours,

(*c*) the poor quality of gas obtained.

The coal supplied to the hopper during each test was carefully weighed and the results are given in the table. It is probable, however, that these figures are considerably less than the actual fuel consumption in each case, as the accumulation of ash prevented some of the fuel from leaving the hopper. For this reason no efficiencies are tabulated, and the ratio of water to coal consumed is probably not correct. The range of the experiments, however, was such that the best ratio of water to fuel must have been used in some of the tests.

The possibilities of the downdraft producer, however, can hardly be said to be exhausted until further experimental work has been done on a grateless producer with bituminous fuels.[17]

[17]A recent article in "Arts et Métiers" (March, 1926) describes producer gas driven trucks by Renault & Panhard respectively, the latter being a downdraft producer. Both machines use wood charcoal as fuel.

SOME TESTS ON A TWO-STROKE CYCLE OIL-ENGINE*

By E. A. Allcut, *Associate Professor of Mechanical Engineering*

During the last few years the two-stroke cycle heavy-oil engine has advanced considerably in popularity for installations where the demand for power is too small to be met satisfactorily by the Diesel engine. Such engines are usually supplied with crank-case compression, and their advantages and disadvantages have already been fully discussed in various publications,[1] so that the main characteristics of this type of engine are well known.

Many of the peculiar features of the two-stroke cycle itself have also been dealt with by Sir Dugald Clerk[2] and other writers. Recent papers dealing with the exhaust, scavenging and charging sections of the cycle have been presented by Illmer,[3] Lanchester and Pearsall,[4] and Morgan,[5] but few records of actual complete tests on engines of this type are available.

The following tests were made to investigate the behaviour of the engine under different loads, to ascertain the extent of the various heat losses and the various efficiencies. As a suitable oil calorimeter was not readily available for student and laboratory work, the experiments described in Appendixes I to III were undertaken with the object of designing such a calorimeter, the result being given in Appendix I (page 16).

Test Arrangements.—The tests were performed on a vertical oil-engine supplied by Messrs. W. H. Allen, Sons and Co., of Bedford, and installed in the Thermodynamics Laboratory of the University of Toronto. It is the standard type of two-stroke cycle heavy-oil engine supplied by this firm, having hot-bulb ignition and crank-case compression. The single cylinder has a bore of 9½ inches, the stroke is 11 inches, and the rated power 25 b.h.p. at a speed of 375 r.p.m. The oil is injected into the cylinder at the proper moment by a pump, the

*By permission of the Council of the Institution of Mechanical Engineers.

[1]Ricardo, "The Internal Combustion Engine," vol. i, pages 218-227, etc.

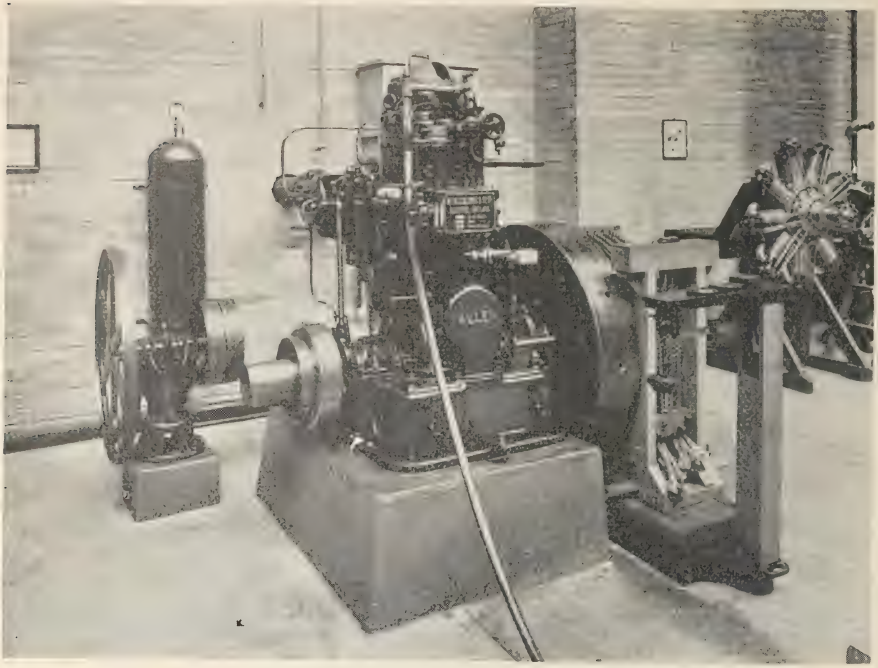
[2]Clerk, "The Gas Petrol and Oil Engine," and various papers.

[3]Illmer, "Porting and Charging of Two-stroke Cycle Engines," S.A.E.J., 1921.

[4]Lanchester and Pearsall, "Certain Aspects of the Two-stroke Cycle," Inst. Auto. Engineers, 1922.

[5]Morgan, "The Charging of Two-stroke Engines," Inst. Auto. Eng., 1923.

Fig. 1.—Two Views of the Arrangement of Oil-Engine for Tests



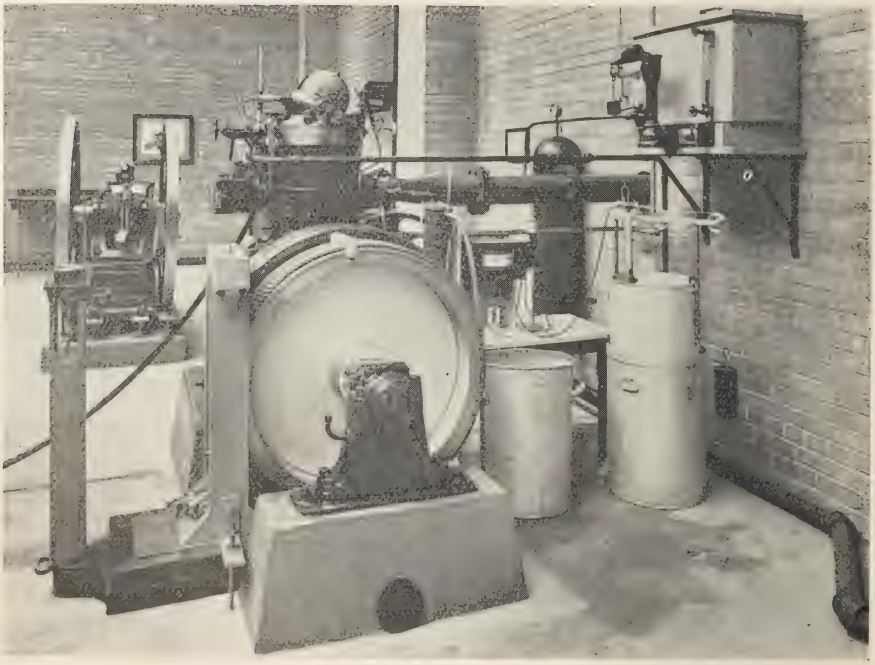
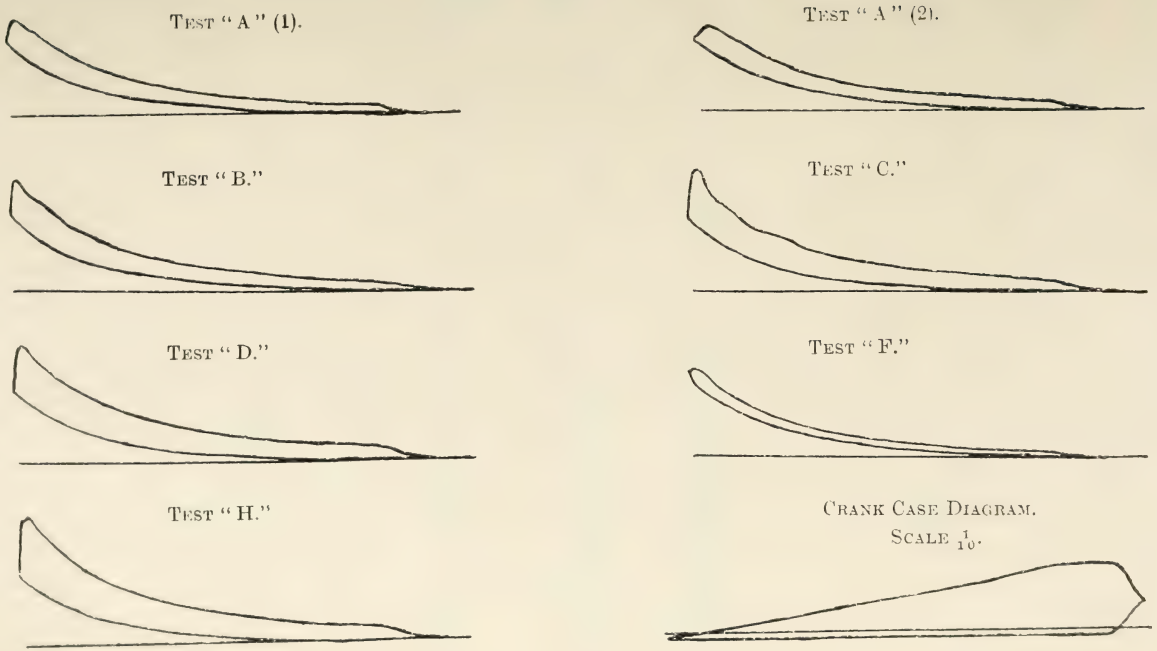


FIG. 2.—OIL-ENGINE TESTS. INDICATOR DIAGRAMS
Scale—320 lb. per inch

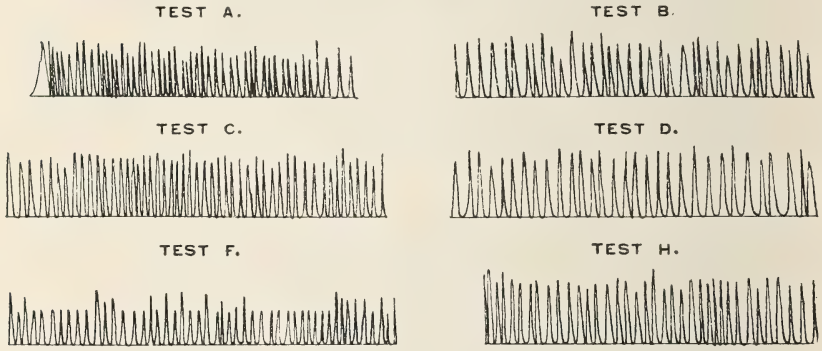


stroke of the plunger being regulated by a governor to keep the speed constant when variations of load occur. The general lay-out and many details of the engine and test apparatus will be seen from the photographs, Fig. 1, and other particulars are embodied in Table I (pages 11-15).

For test purposes the oil was supplied from a tank mounted on a sensitive weighing machine, readings being taken at ten-minute intervals during each test. Curves were plotted from these data, and the rate of oil consumption was found to be constant for each test. In each case the engine was started up on paraffin, was changed over to fuel oil after about ten minutes, and was run for at least sixty minutes under steady conditions before any readings were taken.

FIG. 3.—OIL-ENGINE TESTS. EXPLOSION RECORDS

Scale—640 lb. per inch.



The methods employed for obtaining the calorific value of the oil-fuel are detailed in Appendix I (page 16).

A Crosby gas-engine indicator was connected to the cylinder and numerous experiments were made to ascertain the best strength of spring for these conditions, a rate of 320 lb. to the inch being finally selected.[6] With this the following cards were taken at frequent intervals during each test:—

(*a*) Indicator diagrams for indicated horse-power determinations (Fig. 2).

(*b*) Explosion records to indicate the regularity of combustion about thirty consecutive explosions being recorded on a time base for each card (Fig. 3).

(*c*) Light spring diagrams (1/80 spring) for examining conditions at the end of the stroke. Oscillations due to the high speed made it inadvisable to use a lighter spring for this purpose, (Fig. 4).

[6]Attempts were made to reduce pencil friction by taking the diagrams on smoked cellulcid and paper, but the results obtained were no better.

Another indicator was connected to the passage joining the crank-case to the inlet ports, and diagrams were taken at frequent intervals with a spring rated at 10 lb. per inch. A thermometer was also inserted at this point to indicate the mean temperature of scavenging, and owing to the low compression pressure (3-4 lb. per square inch) and the heavy mass of metal, it is probable that very little cyclical variation of temperature occurs at this point. All springs were calibrated for accuracy by means of a dead-weight gauge-tester. In working out the indicated horse-power it was found necessary to planimeter each diagram at least three or four times to ensure the maximum possible accuracy for the mean effective pressure.

The brake used was an ordinary rope-brake mounted on a platform weighing machine, and its construction will readily be seen from the photographs (Fig. 1). In the preliminary experiments it was found that with this type of brake loads less than 13 b.h.p. could not be carried steadily, and therefore this formed the lower limit of test range. No-load tests were made by removing the brake.

The engine ran very steadily throughout and care was taken to keep the load constant during each test, a man being kept constantly at the brake for that purpose. The exhaust temperatures were measured by means of a calibrated Chromel-Copel thermo-couple inserted in the exhaust pipe as close to the engine as possible, and during each test the variation of temperature was usually not greater than 10° to 20° F.

A sample of exhaust gas was taken from the exhaust-pipe close to the thermo-couple by means of a small tube closed at the end and drilled with a large number of small holes for the purpose of obtaining a sample as representative as possible. This was taken through a water-cooled spiral, the condensate being collected in U-tubes containing calcium chloride, and the dried gas received in a calibrated gas-holder containing a thermometer and pressure-gauge. The holder had a capacity of 2 cubic feet, and its rate of rise was controlled in such a way that this quantity of gas had accumulated at the end of each ninety-minute test, after which samples for analysis were immediately transferred to glass sampling tubes of the usual kind. The gas analysis apparatus used was that known as Burrell's apparatus, and is described in the United States Bureau of Mines Bulletin, No. 42.

The cooling water was collected in tanks mounted on platform weighing-machines and the inlet and outlet temperatures were measured. The quantity was controlled in each test to give an outlet temperature as near as possible to 135° F. The speed of the engine in all tests was taken every ten minutes on the main shaft by means of a speed counter, and great care was taken to ensure the accuracy of this measurement.

Test Results.—Typical indicator diagrams, explosion records and

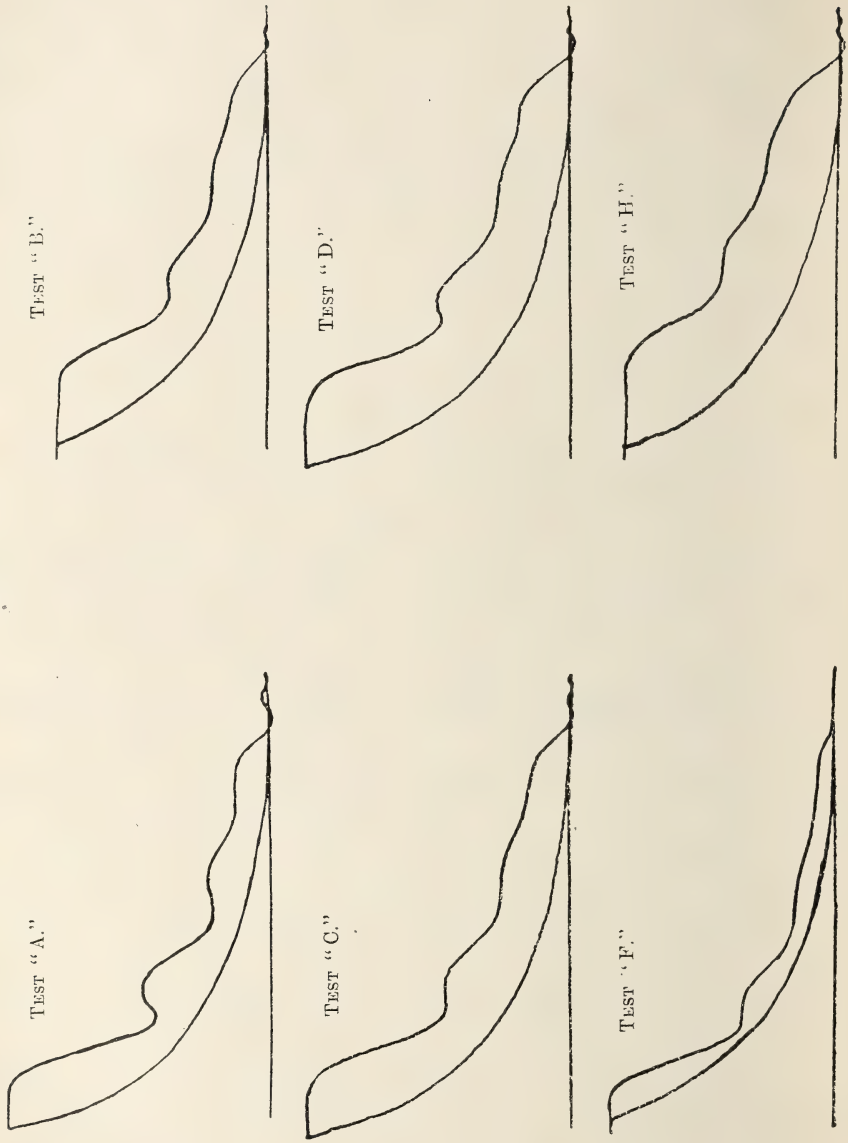
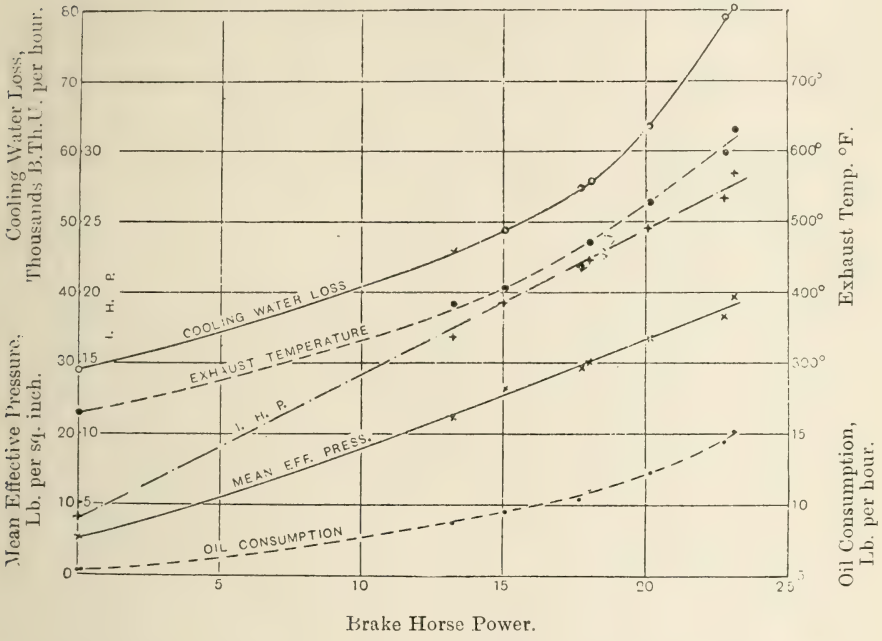


FIG. 4.—OIL-ENGINE TESTS. LIGHT SPRING DIAGRAMS
Scale—80 lb. per inch

light spring diagrams are shown in Figs. 2, 3 and 4 respectively, and the various numerical quantities relating to them are given in Table I. The coefficient n in the formula $PV^n = \text{Constant}$ varies from 1.13 to 1.04 in the case of expansion curves, the lower values being characteristic of the heavier loads. The form of the compression curve varies little, the average value of n being 1.33. From the light spring and crank-case diagrams it is evident that the compression curve starts practically from atmospheric pressure at all loads, but a large number of cards

FIG. 5



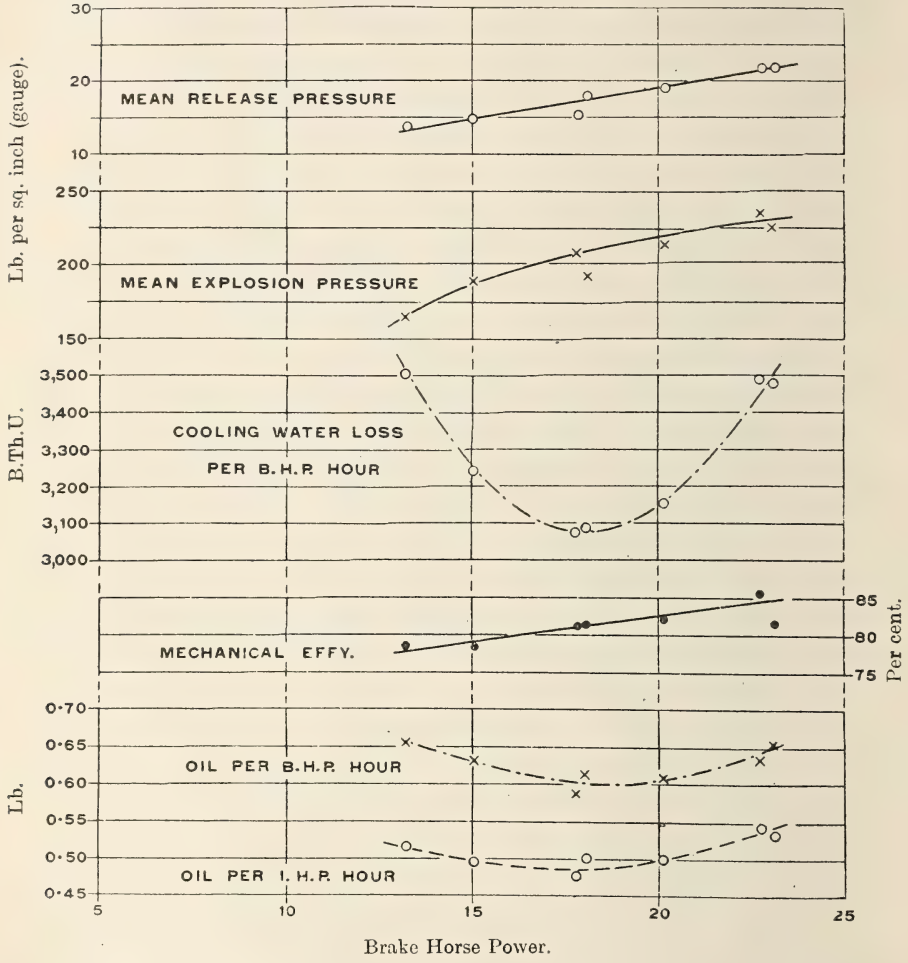
indicate oscillations of pressure during the exhaust period (Fig. 4, Tests C, D, H).

This engine is governed by restricting the supply of oil to the cylinder at light loads, and in the no-load test it was observed that frequently no firing took place. If this occurred while indicator diagrams were being taken, the pencil was kept on the paper until a diagram was obtained, and the mean effective pressure worked out for all these diagrams in the usual way. The explosion records were then used to establish the ratio of firing to total cycles, and the figure obtained by multiplying the mean effective pressure already obtained by this factor was considered to be the true mean effective pressure at no load.

In this test the percentage of "misses" was 64.4 of the total number

of cycles, and the indicated horse-power thus obtained was 4.02. Deducting 1.48 for crank-case compression, the net indicated horse-power was 2.54, a value very close to the differences between indicated horse-power and brake horse-power in the other tests.

FIG. 6



At heavy loads the combustion is practically at constant volume, but at light loads many cards show slow combustion on account of the poorness of the charge (*cf.* Fig. 2, Test "A" 2). A number of preliminary tests were made before the present series, and in these it was observed that late ignitions frequently occurred. The injection was

therefore advanced about 6 deg., the fuel consumption in the present series being less than that in the preliminary tests as follows:

Test	A	C	D	E
	Per cent.	Per cent.	Per cent	Per cent.
Reduction in oil consumption	14	8.5	7.5	0

After this adjustment had been made no late ignitions were observed on any of the diagrams.

The mechanical efficiencies vary from 78 to 85 per cent. and the thermal efficiencies from 24 to 27 per cent. (Table I, and Fig. 6). In the calculation of the loss of heat to exhaust, allowance was made for the heat lost in supplying kinetic energy to the exhaust products leaving the cylinder immediately after the uncovering of the ports. For this purpose a "fill efficiency"[7] of 0.6 was used and adiabatic expansion through the ports assumed. As the total amount of heat thus dissipated is comparatively small (3 to 4 per cent.) no great inaccuracy is likely to arise from these assumptions. The amount of heat unaccounted for in the heat balance varies from 8 to 10 per cent. This includes radiation and any oil escaping unburned through the ports. No carbon monoxide was detected in the exhaust gases in any of the tests.

In the no-load test, however, this discrepancy is large, and it is fairly evident that when explosions are missed oil is delivered to the cylinder in insufficient quantity to form an explosive mixture, and thus the fuel escapes through the ports. This would account for the large percentage of missing heat.

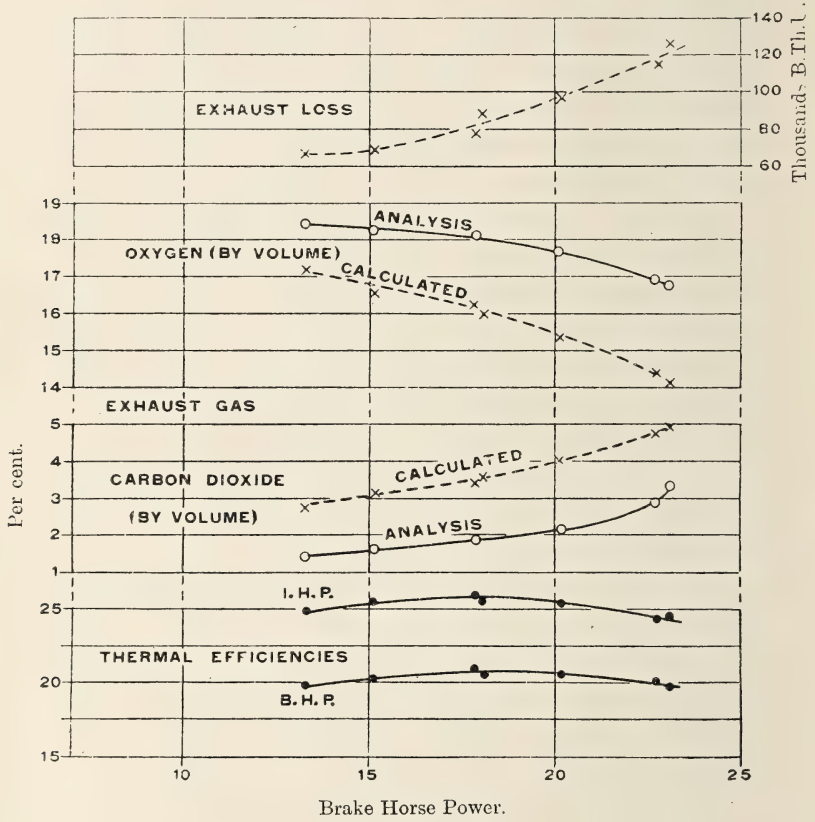
The exhaust analyses obtained in the manner already described (page 7) present some features of interest. The first set of analyses showed low percentages of carbon dioxide, and on investigation this was found to be due partly to the presence of free lime in the calcium chloride used for drying purposes. This was remedied, and the analyses shown in Table I (Section 19*e*) were obtained. Calculations were then made of the weight of carbon delivered to the engine and the weight leaving it as shown by the exhaust analyses, and the following table shows the percentage of carbon accounted for by the exhaust gas analyses:

Test	A	B	C	D	E	G	H
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Percentage of carbon accounted for	51.3	50.5	53.4	52.8	60.7	51.7	67.7

[7]Illmer, Porting and Charging of Two-stroke Engines," A.S.M.E., 1921.

This discrepancy is due to the fact that the first puff of exhaust gas leaving the cylinder at a high velocity is comparatively rich in carbon dioxide, and as the sample is collected at a constant velocity, the proper proportion of carbon-rich gas does not appear in the sample. For this reason Table I (Section 23) and Fig. 7 are supplemented by corrected values of carbon dioxide and oxygen content, obtained by calculation

FIG. 7



from the weights of air and oil delivered to the cylinder per cycle and assuming complete combustion. The other results contained in Table I and plotted in Figs. 5, 6 and 7 are self-explanatory, and do not call for particular comment.

In conclusion, the author wishes to express his thanks to the authorities of the University of Toronto, and particularly to Professors R. W. Angus, J. W. Bain, and O. W. Ellis for the use of apparatus and other valuable help. The oil analyses and Parr Calorimeter tests were made

TABLE 1

1. Type of Engine:—Heavy Oil

2. Description:—Two-stroke, crank-case compression, hot-bulb ignition, single acting, single cylinder, vertical.

3. Rated Power:—25 B.H.P.

4. Cylinder Diameter:—9½ inches.

5. Stroke:—11 inches (0.917 feet).

6. Constants:—Compression volume, 129.7 cu. in. (0.075 cu. ft.).
Stroke volume, 778 cu. in. (0.45 cu. ft.).
Compression ratio, 5.8.
Crank-case volume, maximum, 2.387 cu. ft.
" " minimum, 1.937 cu. ft.
I.H.P. constant for 1 lb. m.e.p. and 1 r.p.m. 0.001975.
Air-cycle efficiency, 51.3 per cent.

7. Test No.	A	B	C	D	E	F	G	H
8. Date	21/7/24	24/7/24	21/7/24	25/7/24	24/7/24	25/7/24	29/7/24	29/7/24
9. Duration of test ..... minutes	90	90	90	90	90	90	90	90
10. Atmospheric conditions:								
(a) Barometer ..... inch	29.82	29.48	29.80	29.50	29.48	29.50	29.76	29.76
(b) Wet bulb thermometer ..... °F.	77	74.5	78.5	74.4	77	74.5	75.8	78.3
(c) Dry bulb thermometer ..... °F.	84	80.5	86.5	79.2	82	86	80	83.4
(d) Humidity ..... per cent.	73.2	77.2	70.0	80.3	80.2	58.6	82.6	80.2
(e) Lb. water per lb. dry air	0.0188	0.0175	0.0194	0.0174	0.0191	0.0169	0.0184	0.0198

TABLE 1—(*continued*)

11. Fuel Quality:								
(*a*) Sp. Gr. at 74.8° F.	0.849 (Average sample)	..	..	..	..	..	..	..
(*b*) Viscosity	See below (Appendix)	..	..	..	..	..	..	..
(*c*) Cal. value (higher)	B.Th.U. per lb.19,850	..	..	..	..	..	..	..
(*d*) " (lower)	B.Th.U. per lb.18,715	..	..	..	..	..	..	..
(*e*) Carbon.....per cent.	85.45	..	..	..	..	..	..	..
(*f*) Hydrogen..... "	13.01	..	..	..	..	..	..	..
Flash Point 186° F. A								
Flame Point 202° F. A								
12. Fuel Quantities:								
(*a*) Weight per hour.....lb.	8.71	9.52	10.44	12.27	14.40	5.28	11.07	15.14
(*b*) " per b.h.p. hour..... "	0.653	0.631	0.586	0.609	0.633	..	0.613	0.655
(*c*) " per i.h.p. hour..... "	0.516	0.494	0.476	0.499	0.541	1.313	0.498	0.533
13. Speed r.p.m.	382.1	370.0	380.7	370.6	367.3	380.5	373.3	364.3
14. Brake particulars:								
(*a*) Diameter of drum.....ft.	3.11	..	..	..	..	..	..	..
(*b*) Brake radius (mean)..... "	1.586	..	..	..	..	..	..	..
(*c*) Brake constant	0.000302	..	..	..	..	..	..	..
(*d*) Gross load.....lb.	160	180	200	225	250	..	205	255
(*e*) Net load..... "	115	135	155	180	205	..	160	210
(*f*) B.H.P.	13.27	15.08	17.81	20.15	22.74	..	18.04	23.10
15. Indicator Diagrams:								
(*a*) Mean explosion pressure.....lb.	164	190	209	214.2	235	..	192	225
(*b*) " compression pressure..... "	128	128	128	128	128	128	128	128
(*c*) " release pressure..... "	13.8	14.8	15.2	18.8	21.6	..	17.9	21.9
(*d*) " effective pressure..... "	22.40	26.45	29.20	33.6	36.70	5.35	30.16	39.50
(*e*) Gross i.h.p.	16.89	19.28	21.95	24.59	26.63	4.02	22.24	28.40
(*f*) M.E.P. crank-case.....lb.	1.91	1.85	1.79	2.15	2.03	1.97	2.19	2.23
(*g*) Max. pressure crank-case..... "	3.65	3.50	3.60	3.80	3.70	3.60	3.90	3.90
(*h*) I.H.P. crank-case	1.44	1.35	1.34	1.57	1.47	1.48	1.61	1.60
(*k*) Net i.h.p.	15.45	17.93	20.61	23.02	25.16	2.54	20.63	26.80

PLATE 1—*(continued)*

	A	B	C	D	E	F	G	H
Test No.								
Date	21/7/24	24/7/24	21/7/24	25/7/24	24/7/24	25/7/24	29/7/24	29/7/24
16. Mechanical efficiency.....per cent.	78.5	78.4	81.2	81.9	85.5	..	81.2	81.3
17. (a) Temperature in crank-case.....°F.	102	99	104.5	99.5	103.3	101	98.4	103.6
(b) Suction in crank-case.....lb.	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
18. Cooling water:								
(a) Quantity per hour.....lb.	697.7	672.8	678	788.7	952.8	359	664.5	961.3
(b) Inlet temperature.....°F.	58.5	61.9	58.5	56.4	58.8	60.5	59.1	56.2
(c) Outlet temperature..... "	135	134.4	139.3	136.9	142	140.2	142.9	139.7
(d) B.Th.U.....per hour	46,489	48,778	54,782	63,494	79,273	28,612	58,685	80,268
(e) B.Th.U. per b.h.p..... "	3,503	3,234	3,076	3,151	3,486	..	3,087	3,475
(f) " per i.h.p..... "	2,752	2,530	2,496	2,574	2,977	7,117	2,594	2,826
19. Exhaust Gases:								
(a) Temperature in exhaust pipe....°F.	385	495	435	525	598	230	470	630
(b) Temperature after cooling..... "	81.4	79.5	79.7	..	78	..	77.1	75.1
(c) Gas collected in holder.....cu. ft.	1.98	1.685	1.81	1.96	1.815	1.63	1.85	1.85
(d) Exhaust loss, B.Th.U.....per hour	66,520	69,180	78,559	97,480	115,190	..	88,900	127,180
(e) Analysis: CO_2 .....per cent.	1.49	1.59	1.80	2.11	2.86	0.7	..	3.33
(f) " O_2 "	18.43	18.25	18.10	17.70	16.90	19.9	..	16.73
Volume CO "	..	..	..	..	..	..	..	..
" N "	80.17	80.16	80.10	80.19	80.24	79.4	..	79.94

TABLE I—(*continued*)

20. Efficiencies, etc.:								
(*a*) B.Th.U. consumed.....per hour	172,890	188,970	207,230	243,560	285,840	104,810	219,740	300,530
(*b*) B.Th.U. per b.h.p..... "	13,028	12,531	11,629	12,086	12,570	..	12,180	13,010
(*c*) Thermal efficiency on b.h.p. basis per cent.	19.50	20.27	21.83	21.00	20.21	—	20.87	19.53
(*d*) B.Th.U. per i.h.p. . . hour	10,236	9,801	9,441	9,904	10,732	26,072	9,880	10,581
(*e*) Thermal efficiency on i.h.p. basis per cent.	24.79	25.89	26.87	25.63	23.64	9.74	25.69	24.00
21. Heat balance per cent. I.H.P.	24.79	25.89	26.87	25.63	23.64	9.74	25.69	24.00
Cooling water.....	26.88	25.81	26.44	26.07	27.73	27.30	26.70	26.71
Exhaust.....	38.48	36.61	37.91	40.00	40.30		40.45	42.31
Radiation and unaccounted for.....	9.85	11.69	8.78	8.30	8.33	A62.96A	7.16	6.98
22. Volumetric efficiency of pump....per cent.	79	77.8	77.1	78.8	79.2	74.8	80	81.2
23. Corrected analysis ACO_2.....	2.75	3.15	3.4	4.03	4.75	..	3.54	4.93
(by vol.) of exhaust AO_2.....	17.20	16.55	16.25	15.35	14.40	..	16.00	14.12
gases (calculated) AN_2.....	80.05	80.30	80.35	80.62	80.85	..	80.46	80.85
24. Mean valve of "n" (expansion).....	1.12	1.11	1.12	1.10	1.06	1.12	1.13	1.04
" " " (compression).....	1.334	1.334	1.334	1.334	1.334	1.334	1.334	1.334

by Professor L. J. Rogers, and Messrs. J. S. E. MacAllister and F. W. Watson assisted very materially in preparing drawings and in the actual experimental work respectively.

The paper is illustrated by 7 Figs., and is accompanied by 4 Appendixes with 10 Figs.

APPENDIX I

THE CALORIFIC VALUE OF OIL

In all experiments involving the use of liquid fuels accurate measurement of the calorific value of the fuel is a matter of great importance. The best method of measuring this property was carefully considered in connection with the preceding series of tests. The sample of oil was taken by means of a glass tube extending from the top to the bottom of the tank in each instance, so that a vertical section of the contents was obtained.

This sample was tested in four different ways:

(1) by a chemical analysis from which the calorific value could be calculated.
(2) in a Mahler Bomb Calorimeter,
(3) in a Parr Calorimeter,
(4) in a special calorimeter described below.

The disadvantages of chemical analysis are that the process is long and complicated, demands great care, a skilled chemist, and special apparatus.

The Mahler Bomb Calorimeter is probably the most accurate apparatus for determining calorific values, but in the case of oil, the quantity burned (about 0.5 gramme) is so small that serious inaccuracies are liable to creep in. High pressures of oxygen must be used, and the fuel is burned under constant volume conditions. In the present series of tests trouble was experienced at first in obtaining consistent results, until it was found that in some cases the thermometer accidentally touched the side of the bomb, and a special attachment was made to control its position.

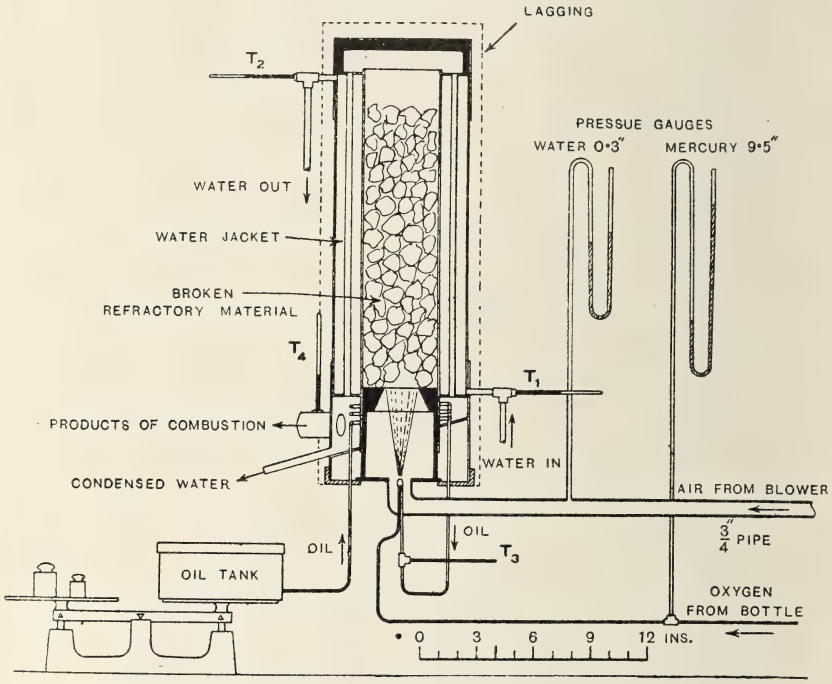
The Parr Calorimeter is convenient for commercial testing, but on account of the smallness of the sample and other difficulties, consistent results are not at all easy to obtain.

It was considered that if an oil calorimeter could be designed on a similar principle to that used in the Junkers and Sargent Calorimeters, well known and widely employed in gas calorimetry, some of these difficulties might be overcome and a closer approximation to the actual

conditions of practice obtained. One method of doing this has been described by Moss and Stern,[8] but suitable burners were not available in the present series of tests, and the fuel to be tested was more difficult to evaporate and inflame than were the petrol, benzene and paraffin used in their apparatus. It was considered that the use of an incandescent surface of refractory material inside the calorimeter body (as

FIG. 8.—*Diagram of Oil Calorimeter.*

T_1.— Temperature of cooling water entering calorimeter.
T_2. ,, ,, ,, ,, leaving ,,
T_3. ,, ,, oil entering calorimeter.
T_4. ,, ,, products of combustion.



used in the "Bonecourt" surface combustion principle) might provide a means of overcoming some of the difficulties, and a calorimeter was designed and constructed on these lines.

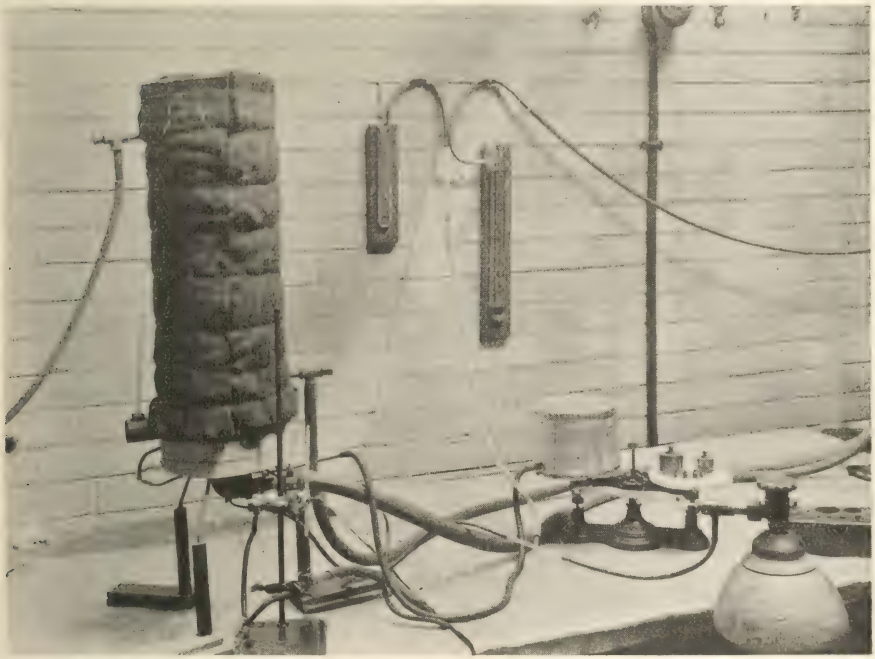
The body of the calorimeter (Fig. 8) consisted of a copper vessel 14 inches long and 4 inches diameter, packed with calcined magnesite, the oil-burner being introduced through an orifice in the bottom. The oil and air mixture was intended to burn on the surface of the refractory material, and the products of combustion returned to the bottom through water-jacketed tubes to an outlet in the usual way. The top and bottom

[8] *Engineering*, 15 December, 1922. Also Harwood in *Engineering*, 28 September, 1923.

of the calorimeter were made removable to facilitate cleaning of the tubes if and when necessary. The water was passed through a jacket at a constant rate, its weight, inlet and outlet temperatures being recorded.

The oil-burner first used was of the Wallsend-Howden type, consisting of two jets delivering tangentially into a whirling chamber before issuing from the final orifice. The air supply was delivered from a small Roots blower.

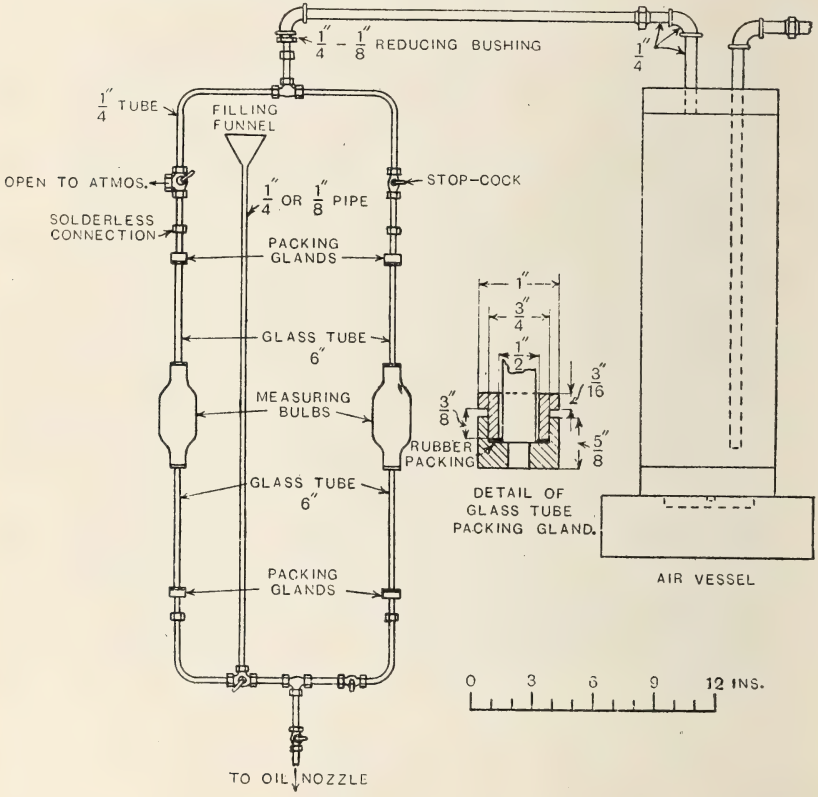
FIG. 9.—OIL CALORIMETER



The pressure necessary for atomizing and delivering the oil was obtained by means of an air vessel (Fig. 10) supplied with water from the town main. The air compressed in this vessel was used as a transmitting medium to apply pressure to the oil in the measuring bulbs. A suitable arrangement of valves permitted either of the two bulbs to be used at will, and a standpipe and funnel enabled one bulb to be filled while the other was delivering a measured quantity of oil to the calorimeter. Accuracy of measurement was obtained by filling each bulb to a mark on the upper glass tube and noting the time taken for the level to fall to a similar mark on the lower tube. Care was taken in design and construction to avoid air and oil pockets.

This method of measurement was abandoned at the conclusion of the experiments described in Appendix II, as it was found that atomization conditions suitable for calorimetric work were difficult to control with a high pressure jet. It was then decided to adopt the principle of introducing air or some other gas into the oil jet, so that good atomization and proper admixture of combustible and supporter of combustion might be obtained.

FIG. 10.—PIPING LAYOUT FOR OIL CALORIMETER HEAVY-OIL RESEARCH



For this purpose an atomizing sprayer of the type used in medical work was obtained, the oil suction pipe being connected by rubber tubing to a supply tank mounted on weighing scales (Figs. 8 and 9). Air was first supplied under pressure, but although the refractory material inside the calorimeter was heated to redness before turning on the oil-jet, satisfactory combustion could not be obtained. An oxygen tank was then connected up to the air jet through a needle-valve, by means of which the pressure could be regulated to any desired extent. This failed to give satisfaction until extra air was supplied to

the outside of the jet by means of a motor driven blower. After a number of experiments had been made it was found that preliminary heating of the refractory material could be dispensed with, the oxy-air-oil jet being easily ignited by a piece of burning paper. If the air and oxygen supply were properly regulated, a perfectly smokeless exhaust could be obtained, and Table 2 gives the results obtained in five successive tests made on the fuel oil used for the engine trials described in this paper.

TABLE 2.—TESTS ON OIL CALORIMETER

Test No.	11	12	13	14	15	16
Duration....mins.	28.45	28.62	23.80	26.73	26.62	20.08
Weight of oil....lb.	0.265	0.265	0.221	0.265	0.265	0.132
Temp. of oil....°F.	87.2	89.0	89.1	96.0	96.3	77.1
Temp. of air....°F.	70.1	71.4	72.8	76.2	77.1	71
Rise of cooling water temp. °F.	14.21	13.98	14.16	14.54	14.48	15.14
Pressure of oxygen ins. mercury	9.51	9.50	9.83	9.80	9.87	9.60
Pressure of air....ins. water	0.3	0.36	0.4	0.38	0.4	0.3
Exhaust gases volumetric composition CO_2	12.55	12.72	11.65	13.87	13.65	10.93
Exhaust gases volumetric composition O_2	8.22	8.00	9.12	6.50	6.48	5.46
Exhaust gases volumetric composition CO	0.0	0.0	0.0	0.0	0.0	0.0
Exhaust gases volumetric composition N_2	79.23	79.28	79.23	79.63	79.87	83.61
Air used per lb. oil....lb.	16.4	16.1	17.7	14.8	15.2	19.8
Oxygen used per lb. oil....lb.	1.02	1.02	1.01	0.97	0.87	..
Total heat developed. B.Th.U	5,262	5,264	4,395	5,252	5,168	2,584
Cal. value of oil (higher) B.Th.U. per lb.	19,850	19,860	19,880	19,810	19,500	19,500
Cal. value of oil (lower) B.Th.U. per lb.	18,715	18,725	18,745	18,675	18,365	18,365

TEST RESULTS ON MAHLER BOMB CALORIMETER

Higher cal. value—B.Th.U. per lb..... 20,034
" " " " ..... 19,947 } Mean value 20,046
" " " " 20,158

TEST ON PARR CALORIMETER—19,850 B.Th.U. per lb.

(Mean of two tests)

Corresponding tests were made on the Parr and Mahler Bomb Calorimeters, and the results obtained on these instruments are also given. It is considered that the Mahler Bomb results are too high.

FIG. 10

As the air pressure necessary for complete combustion is small (about 0.3 inch water pressure), it is advisable to use a gauge of the differential type. In the apparatus used, excessive air pressures caused

losses by blowing back air and oil past the burner, but this could be avoided by improved construction or by automatic regulation of air and oxygen pressures.

The experimental apparatus described and illustrated had hand regulation throughout, and the drop of calorific value observed in test No. 15 is apparently due to reduced oxygen supply.

A further attempt was made to run on air only, using the same pressures as were found satisfactory with oxygen. The air for atomizing was obtained by running water into a large tank and displacing the air under a pressure of 9 to 10 inches of mercury.

On account of the limited volume of the tank, insufficient time was available to obtain quite steady conditions before readings were commenced, but the results of this test are given in Table 2, Test 16. The exhaust was slightly hazy, so that combustion was probably not quite complete. The low cost and greater flexibility available with the use of oxygen, however, make the use of that gas preferable wherever possible.

APPENDIX II

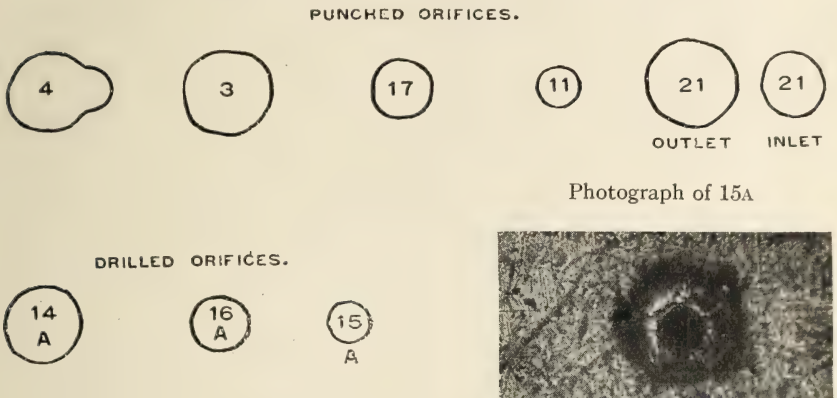
Flow of Oil Through Small Orifices.—In selecting nozzles for an oil calorimeter, the choice is restricted by the fact that with apparatus of a reasonable size only a limited amount of heat can be carried away by the cooling water in a given time. For this reason the nozzle employed must be able to pass a small quantity of oil at a uniform rate, and this involves the use of small orifices. In the Wallsend-Howden type nozzle previously referred to, the diaphragm holes were made 0.0405 inch diameter, and the final orifice 0.016 inch diameter, these being the smallest sizes that could be drilled. On experimenting with a measured quantity of oil, it was found that the escape of oil was far too rapid for practical purposes. The outlet orifice was therefore partly closed by a screw-down needle valve, but this method proved unsatisfactory.

The next procedure was to drill the outlet orifice to a larger size and to substitute for the diaphragm a thin brass sheet with a punched or drilled orifice in its centre. These orifices were made of various sizes and were tested under oil pressures varying from 53 to 12 lb. per square inch. The method of testing was to fill the left-hand measuring bulb (Appendix I, Fig. 10) with oil to a given mark and to time by stop-watch the passage of a known volume of oil through the orifice. From these readings a pressure-time curve was drawn in each case, and from these curves the rates of discharge and the coefficient of discharge were calculated for each orifice at the various pressures employed.

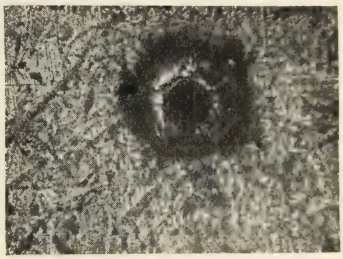
The punched orifices were made in brass 0.013 inch thick by perforating it with a fine sewing needle. At first, orifices similar to No. 4, Fig. 11, were obtained, but by restricting the depth of perforation and rotating the needle, orifices Nos. 3, 17 and 11 were obtained.

The shape and size of the outlet end of each orifice were obtained by means of a photomicrographic apparatus set to magnify 100 diameters.

FIG. 11.—MAGNIFICATION 50 DIAMS. (HALF-SIZE ORIGINALS)



Photograph of 15A



The image of the orifice was thrown on the ground glass focussing screen, traced on paper, and the area obtained by planimeter. This area divided by 10,000 was the actual outlet area of the orifice. The kind of image obtained is shown in the photograph of drilled orifice No. 15A (Fig. 11).

The drilled orifices were made in brass sheets 0.015 inch thick, the smallest obtainable having a diameter of 0.00438 inch. These were preferred to the punched orifices, as they were more easily reproducible and more uniform in section, but tests were made on both.

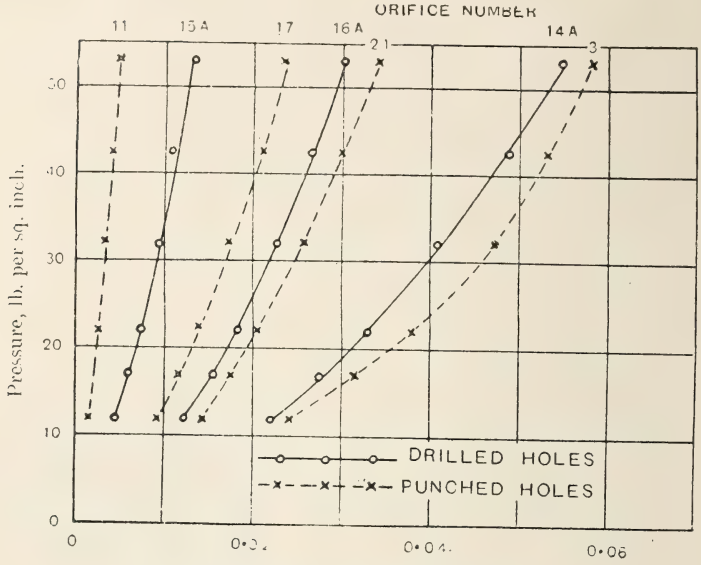
The oil used was that employed in the oil engine tests, having a specific gravity of 0.850, and the following viscosity characteristics as obtained on the Saybolt viscosimeter:[9]

Temperature	Time of Efflux for 60 c.c. Oil
°F.	Secs.
120	38.7
100	40
85	42
70	48

[9]See U.S. Government Specification for Lubricants and Liquid Fuels (1924).

FIG. 12.—DISCHARGE OF OIL FROM SMALL ORIFICES

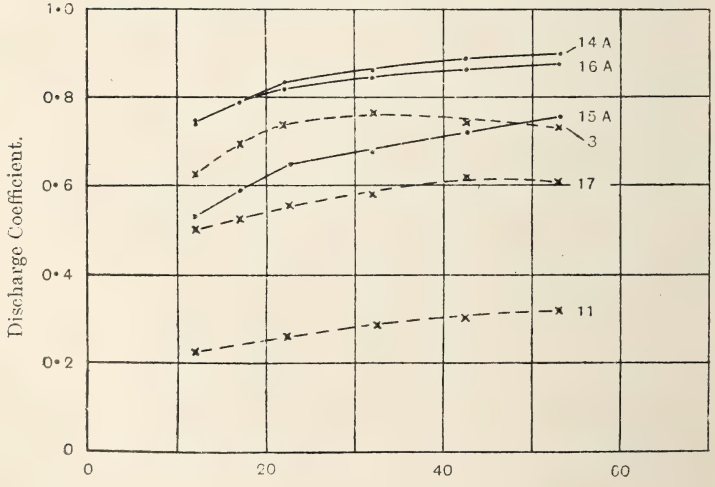
Pressure—Oil Discharged



Oil Discharged, cubic ins. per sec.

FIG. 13.—DISCHARGE OF OIL FROM SMALL ORIFICES

Coefficients of Discharge—Pressure



Pressure, lb. per sq. inch

FIG. 14.—DISCHARGE CURVES FOR DRILLED ORIFICES

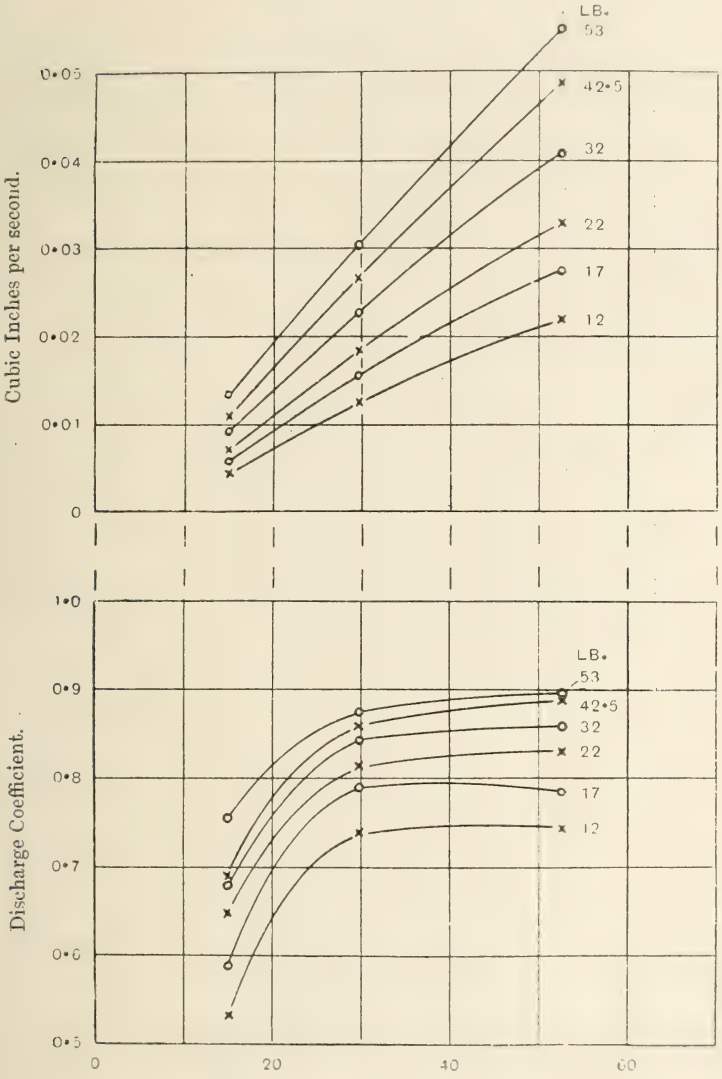
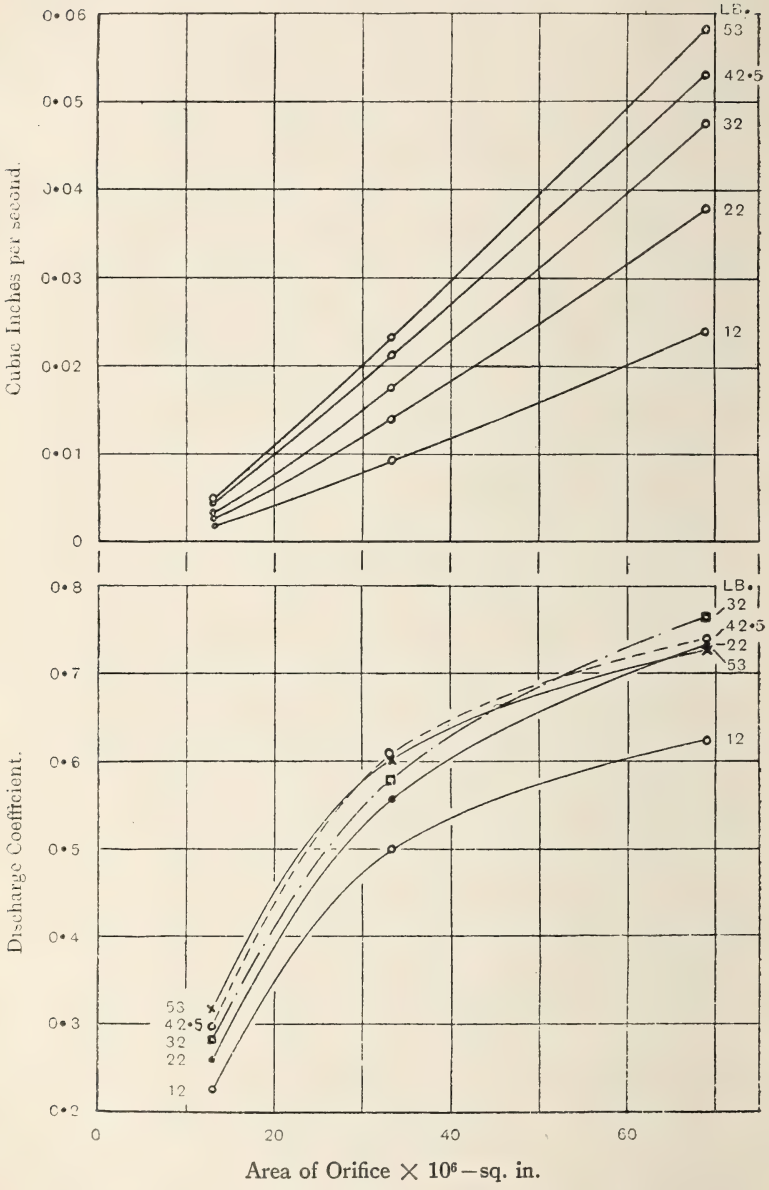


FIG. 15.—DISCHARGE CURVES FGR PUNCHED ORIFICES



Discharge tests at pressures of 53, 42.5, 32, 22, 17 and 12 lb. per square inch respectively were made on each orifice, and the actual rates of discharge (cubic inches per second) for each orifice are plotted in Fig. 12. Coefficients of discharge for each orifice and pressure are plotted in Fig. 13, and it is evident that the curves for both drilled and punched orifices have similar characteristics, but that the coefficients of discharge for punched orifices are lower than those for drilled orifices. It should be noted that these orifices have lengths varying roughly from 1½ to 3½ diameters.

Figs. 14 and 15 are curves connecting orifice areas with fluid discharged for drilled and punched orifices respectively, each curve corresponding to a constant pressure. It will be noted that for orifices having areas less than 0.00003 square inch, the coefficient of discharge decreases very rapidly with the area. For drilled orifices between 0.00003 and 0.00005 square inch, the coefficient keeps approximately constant, but for punched (convergent) orifices the coefficient continues to rise until an area of 0.00007 square inch is reached.

Orifice No. 21 was intended to supply another point on the punched orifice curves, but becoming stopped up during a test, it was opened out on the discharge side, making a divergent orifice (Fig. 11), so that the results are not comparable with those obtained from the other orifices. The curves obtained are similar to those plotted for the other orifices, but the discharge coefficients are higher than those for the convergent punched orifices.

TABLE 3.—DISCHARGE OF OIL FROM SMALL ORIFICES

—		Punched Orifices				Drilled Orifices		
Orifice No		3	17	11	21	14A	16A	15A
Area	sq. in.	0.0000689	0.0000333	0.0000132	0.0000379	0.0000527	0.0000297	0.0000151
Mean diameter	in.	0.00935	0.0065	0.0041	0.00695	0.0082	0.00615	0.00438
Thickness of plate	in.	0.013	0.013	0.013	0.015	0.015	0.015	0.015
Volume of oil discharged, cu. in. per sec.	A53 lb.	0.0581	0.0233	0.00485	0.0341	0.0548	0.0301	0.0132
	A42.5 "	0.0530	0.0211	0.00409	0.0299	0.0487	0.0265	0.01083
	A32 "	0.0476	0.0174	0.00338	0.0257	0.0409	0.0227	0.00924
	A22 "	0.0379	0.0139	0.00257	0.0203	0.0329	0.0182	0.00735
	A17 "	0.0316	0.0116	..	0.0174	0.0275	0.0156	0.00587
	A12 "	0.0241	0.0093	0.00166	0.0143	0.0219	0.0123	0.00448
Coefficient of Discharge	A53 lb.	0.730	0.602	0.316	0.778	0.899	0.874	0.754
	A42.5 "	0.745	0.612	0.298	0.762	0.891	0.860	0.694
	A32 "	0.769	0.580	0.286	0.752	0.862	0.847	0.678
	A22 "	0.738	0.560	0.261	0.718	0.837	0.820	0.653
	A17 "	0.702	0.533	..	0.702	0.797	0.798	0.594
	A12 "	0.634	0.510	0.229	0.685	0.755	0.750	0.541

APPENDIX III

Atomization Tests

In the combustion of liquid fuels atomization plays an important part, and with the successful application of the burner described on page 18, a few experiments were made to ascertain the extent and character of the atomization obtained under different conditions. It had been observed that the atomizing agent (oxygen or air) produced the best results in this case, when a pressure of 10 inches of mercury was used. Tests were therefore made with pressures of 10, 7.6, and 4 inches respectively.

The method of testing was to pass glass slips rapidly across the oil-jet at a distance of about 6 inches above the nozzle. The slips were then placed in an air-tight case, to avoid evaporation or contamination, and were then examined successively under a microscope with a magnification of 30 diameters. Characteristic photographs of the results are shown in Fig. 16, but many more observations were taken to obtain average results.

From the photographs it is evident that the splitting up is by no means uniform, the drops being of various sizes. Fig. 16, D, E, and F, however, show considerable scattering in very small drops—a phenomenon entirely absent from A, B and C. It would appear, therefore, that a pressure of 4 inches of mercury (2 lb. per square inch) is insufficient to produce pulverization into the very small drops obtained at the higher pressures. Also that the higher pressures are only partially successful in this respect.

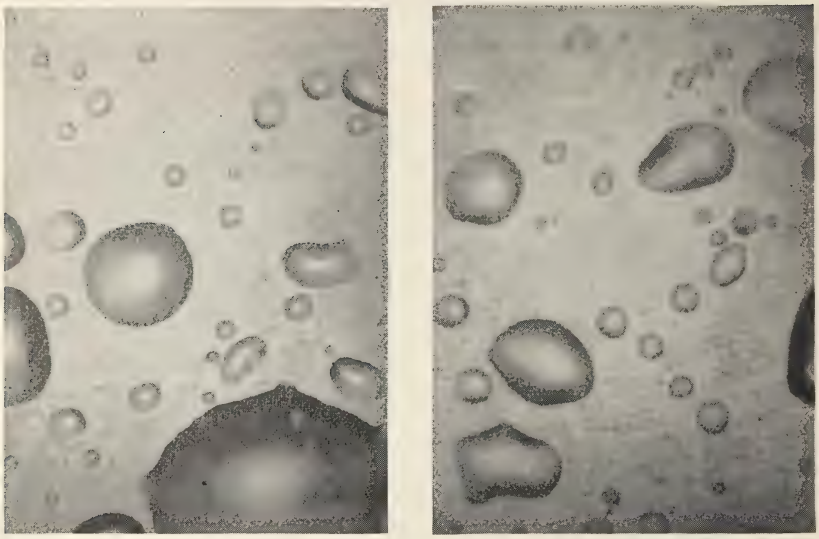
It is interesting to note that the diameters of these small particles vary from approximately 0.0005 to 0.003 inch. These figures, of course, do not indicate the diameters of the original spherical drops, but form a convenient basis of comparison for different methods of atomizing.

The larger drops are still more important, for upon their size depends the possibility of obtaining complete combustion. Although these vary considerably in size, it is possible to get some idea of their mean diameter by going over the entire surface with a microscope and by measuring the diameters of the largest globules in the field of view.

FIG. 16.—ATOMIZATION TESTS, ×30 DIAMS.

Pressure of Oxygen—4 ins. Mercury

(A.) (B)



Pressure of Oxygen—7.6 ins. Mercury

(C.) (D.)

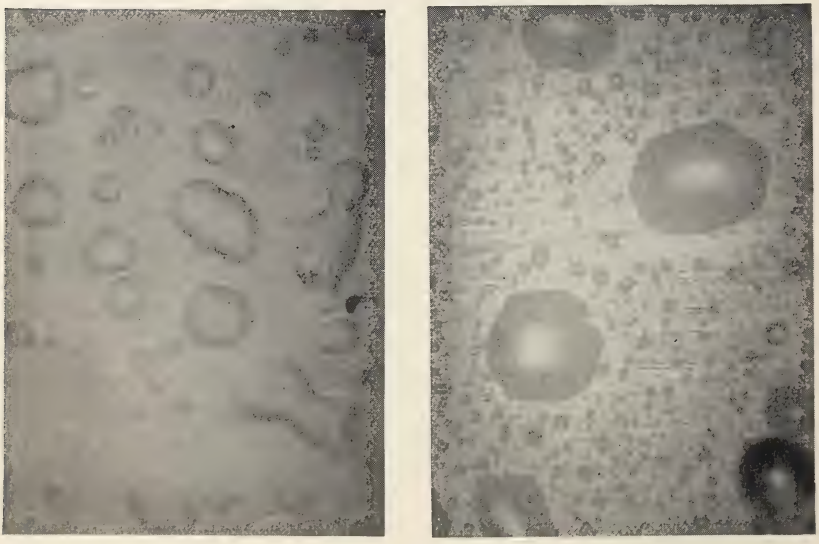
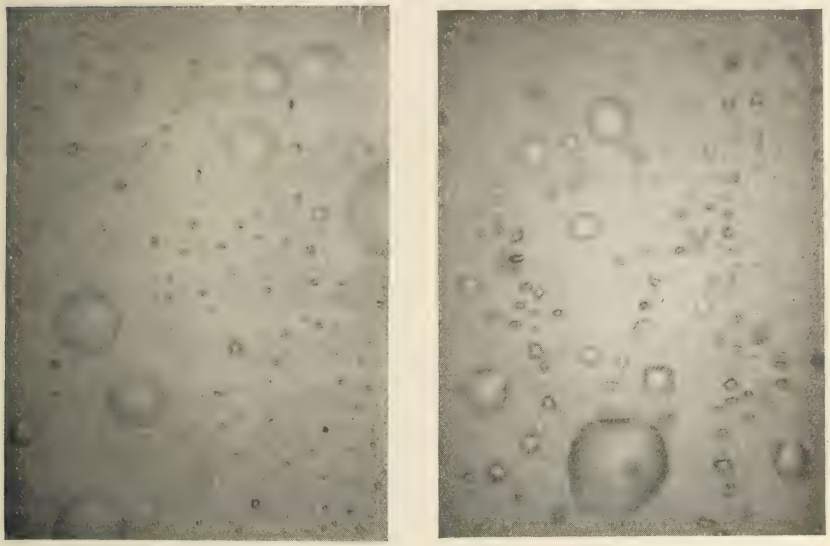


FIG. 16 (continued)—ATOMIZATION TESTS, × 30 DIAMS.

Pressure of Oxygen—10 ins. Mercury

(E.) (F.)



This was done for the three pressures selected, and the results obtained are given in the following table:

Pressure	Diameter of Largest Spot	Average Diameter of Large Spots
	Inch	Inch
10 inch Mercury (A).....	0.0175	0.0098
(B).....	0.0205	0.0088
7.6 inch Mercury (A).....	0.0260	0.0114
(B).....	0.0250	0.0102
4 inch Mercury (A).....	0.0265	0.0130
(B).....	0.0300	0.0153

From these figures it appears that there is a fairly definite relationship between the sizes of the oil globules produced and the atomizing pressure.

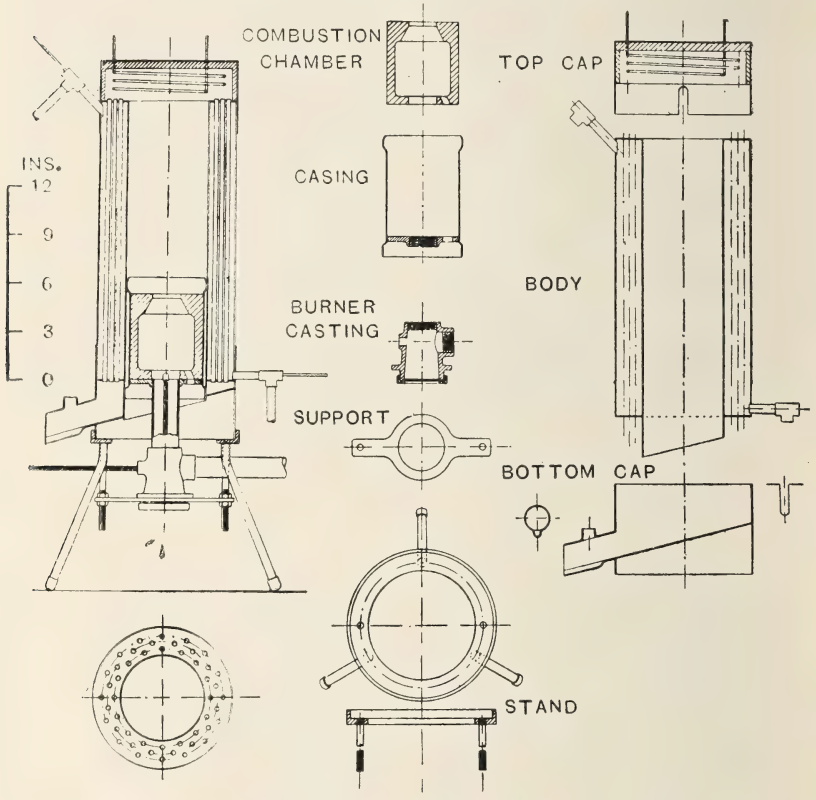
Further experiments along these lines would probably throw more light on the exact nature of this relationship and upon the factors that influence the atomization of liquid fuels generally.

APPENDIX IV

DESIGN AND CONSTRUCTION OF CALORIMETER

As a result of the tests described in Appendix I, a modified design of oil calorimeter was prepared, the details of which are shown in Fig. 17. FIG. 17

FIG. 17.—CALORIMETER FOR HEAVY OILS



The combustion chamber is moulded in carborundum or some other heat-resisting material, and is enclosed in a casing of spun copper, to the bottom of which a flange is brazed. This casing is shaped to form a sliding joint with the inner body tube, and to leave an air space between the combustion chamber and the water jacket. This allows the combustion chamber to become sufficiently hot, but intercepts the heat radiated from its outer surface. A hole is made in the flange and combustion chamber to allow the oil to be lighted while the burner is in position.

The casing, combustion chamber, and refractory filling are supported by a tube screwed into the brass flange at one end and into the burner casting at the other. This casting has a glass window at the bottom, through which the conditions of combustion can be observed, and it also has a flange which rests upon the supporting bridge piece. The latter is held in position by two studs screwed into the stand, so that by adjusting the nuts the position of the combustion chamber relative to the jacket may be altered at will, and also, by taking off the nuts, the whole of the inside of the calorimeter may easily be removed. The air pipe screws into one side of the burner casting, and the oil and oxygen pipes enter through the other side.

The calorimeter body is of the usual water-jacketed type, containing forty-eight tubes, and the outlet water pipe is brazed to it at an angle, as shown, to ensure the jacket being full of water and the outlet thermometer always immersed.

The top cap is removable and contains a coil by means of which heavy oils can be preheated and their viscosity reduced before they reach the burner. This is unnecessary with light oils.

The bottom cap is so shaped that the water of condensation can run freely to the outlet, a lip being formed in the latter to enable the water temperature to be taken if necessary. This cup is soldered to the inner body tube to form a water-tight joint, but by melting out the solder the bottom cap also can be removed to facilitate tube cleaning if and when necessary.

The whole of the body is surrounded with 1 inch thickness of heat-insulating material, and the various connections are made as in the case of experimental apparatus shown in Appendix I, Fig. 8.

THE INFLUENCE OF SPEED ON ENGINE PERFORMANCE*

By E. A. Allcut, *Associate Professor of Mechanical Engineering.*

The following tests were made on a "Climax" tractor engine (Model K) in the Thermodynamics Laboratory at the University of Toronto, and were undertaken to investigate the effect of different speeds on the thermal efficiency, cooling water loss, and other items that influence the performance of this engine.

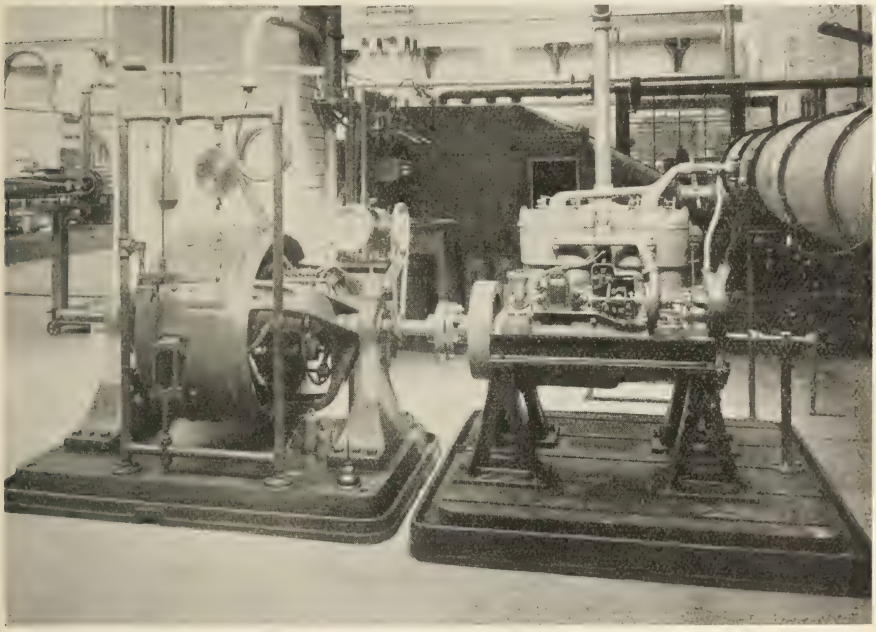


Fig. 1.— Climax tractor engine and Sprague dynamometer.

The engine has four cylinders with side-by-side valves, and was coupled to a Sprague electric dynamometer, the general layout being shown in Fig. 1. The main specifications of this engine are as follows:

Cylinder bore	5 in.
Stroke	6½ in.
Stroke vol	127.4 cu. in.
Clearance vol	49 cu. in.
Compression ratio	3.6
Valve diameter	2½ in.

*"The Automobile Engineer" Aug., 1925.

Valve Timing—Inlet valve opens 11 degrees after dead centre, closes 37 degrees after dead centre; Exhaust valve opens 37 degrees before dead centre, closes 9 degrees after dead centre.

The speed of the engine is controlled by a centrifugal governor

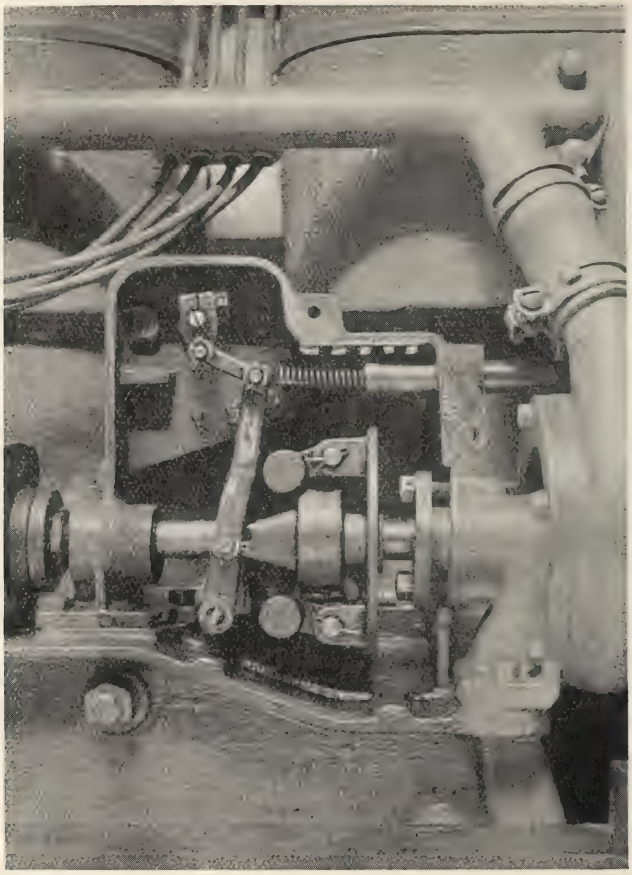


FIG. 2.—Governor gear.

mounted on the pump shaft. This is seen in Fig. 1, but is shown in greater detail in Fig. 2. From this illustration it will be seen that the tension of the governor spring is controlled by a plunger, and above this are four notches into which fits a peg on the side of the plunger. Four different spring tensions may thus be obtained, corresponding to four different speeds of the engine, as follows:

Notch	Speed	Test Nos.
1	500-600	1-4 and 21-25
2	650-740	16-20
3	730-790	10-14
4	780-900	5- 9

As the object of the tests was to observe the influence of this variable alone, all other factors were kept as constant as possible. Accordingly, the outlet temperature of the cooling water was kept at about 170° F., and the settings of air regulator, throttle valve (hand controlled) and

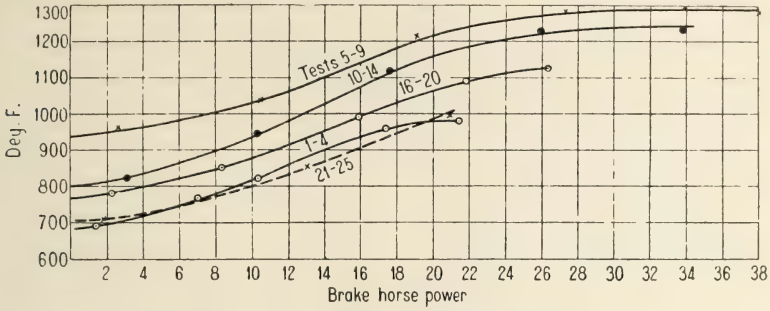


FIG. 3.—Exhaust temperatures.

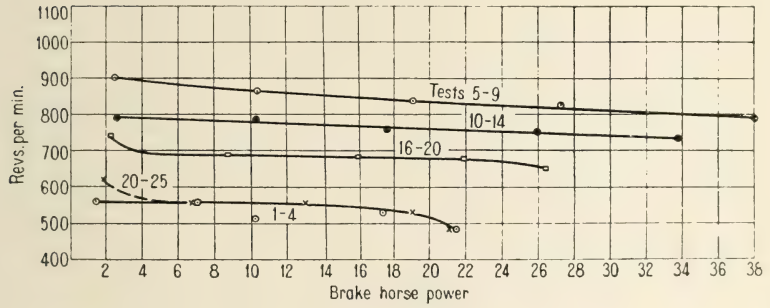


FIG. 4.—Speeds.

ignition were not altered during the tests. It is recognized that, to get the best conditions, ignition should be advanced as the speed rises, but this would have introduced another variable into the conditions, which in this case was not desirable.

The tests were each of 20 to 30 minutes' duration, sufficient time being allowed after the completion of each test to permit the engine to steady down under the new conditions before another experiment was started. In tests 4, 9, and 14, shorter periods were taken as the engine began to fail after about 10 minutes, but in these cases sufficient readings had already been taken to permit the performance of the engine to be ascertained with reasonable accuracy.

The fuel consumption was measured by weight, readings being taken at frequent intervals during each test to enable the uniformity of speed to be observed. The cooling water was supplied from the town mains, and the rate of supply was measured by weighing. The exhaust temperature was obtained by means of a Chromel-Copel thermocouple placed

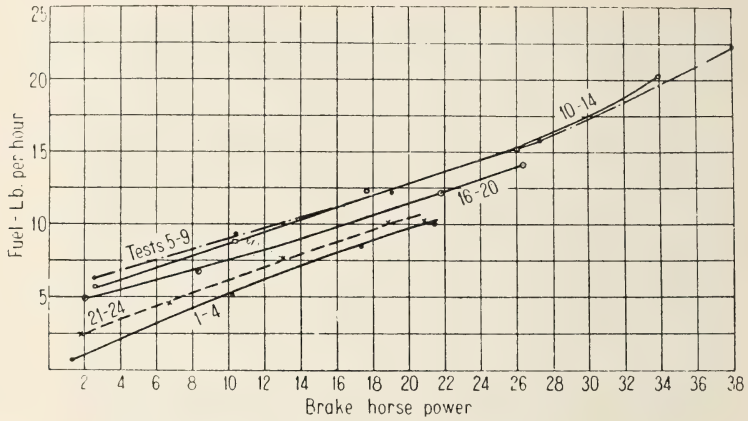


FIG. 5.—Fuel consumption per hour.

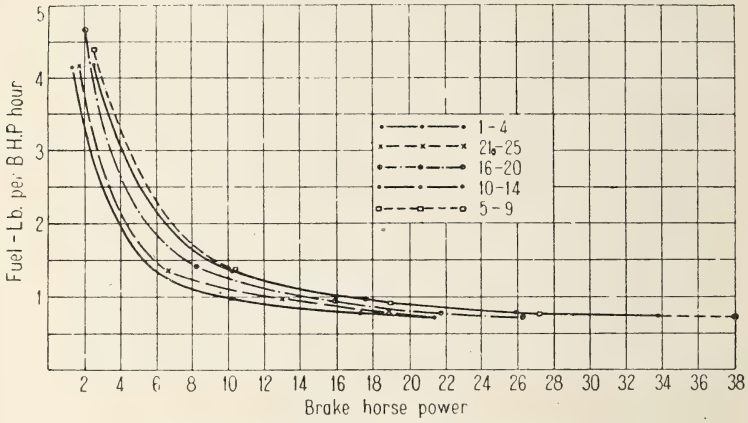


FIG. 6.—Fuel consumption per b.h.p. hour.

in the exhaust manifold at the point where the four exhaust branches join.

The results obtained are given in the accompanying table, and are illustrated by Figs. 3 to 11.

At each speed, a test approximating as nearly as possible to no-load conditions was made by cutting off the field current from the dynamometer. Tests 1 to 4 were first made with the crank case full of oil from

the laboratory stock, but the engine did not run satisfactorily on this, and so, for the other tests, the crank case was supplied with the same quantity of a heavier grade of motor lubricating oil. When a check test was made at the low speed, it was found that the results were different

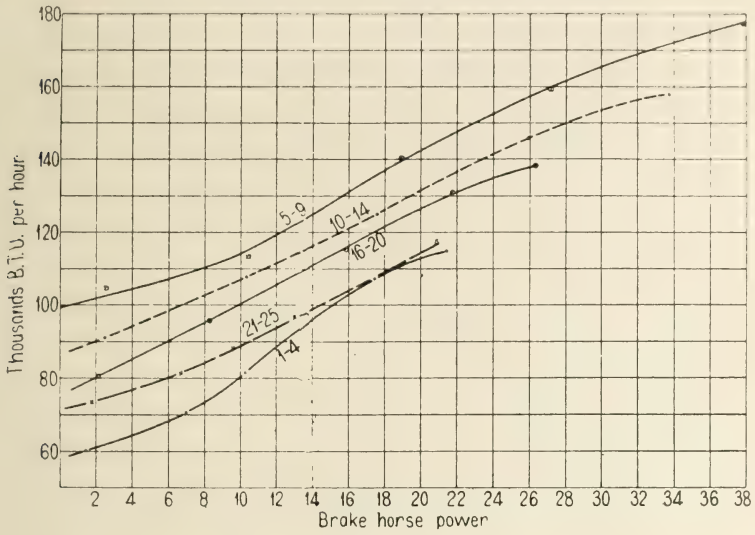


FIG. 7.—Cooling water loss.

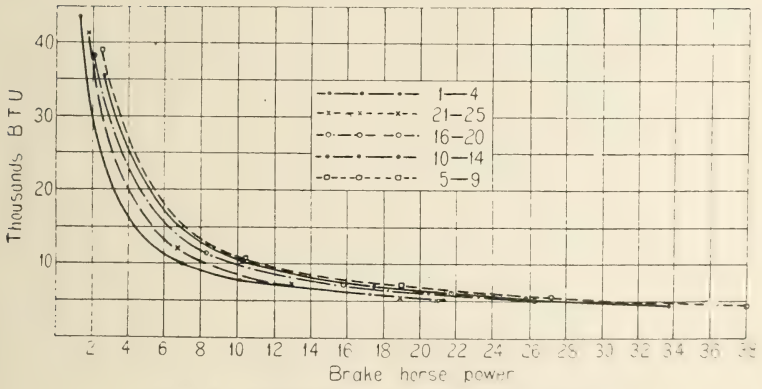


FIG. 8.—Cooling water loss per b.h.p. hour.

from those previously obtained, and so the whole series was repeated in tests 21 to 25, higher fuel consumptions and lower thermal efficiencies being obtained than in tests 1 to 4. As no other conditions were changed, it would appear that these differences were due solely to the greater viscosity of the oil in the crank case, which completely masked any

TEST NO.	2.	1.	3.	4.	21.	23.	22.	24.	25.	16.	17.	18.
Nominal speed r.p.m. (approx.) ..	500	500	500	500	500	500	500	500	500	650	650	650
Air Temp. deg. F.	75·3	77·4	75	72·6	80	84·5	84	91	88	74	78	80
Exhaust Temp. deg. F.	690	820	960	980	705	750	850	970	995	780	850	990
Fuel per hour, lb.	5·72	10·1	13·5	15·0	7·4	9·15	12·65	15·2	15·1	9·93	11·85	15·12
Cooling water per hour, lb. ..	481·5	650	866	906	610	668	745	890	926	598	723	893
,, ,, Inlet Temp. deg. F.	52·5	51·6	47·6	47·5	51·8	50	50·2	48·8	48·4	49·3	49·0	48·7
,, ,, Outlet Temp. deg. F.	177·1	177	171	174·7	172·7	172·1	180·2	173·6	176·1	184·4	181·6	178
,, ,, Temp. rise deg. F...	124·6	125·4	123·4	127·2	120·9	122·1	130	124·8	127·7	135·1	132·6	129·3
,, ,, B.Th.U. per hour ..	60,000	81,510	106,860	115,240	73,750	81,560	96,850	111,070	118,250	80,790	95,870	115,460
Brake load, gross lb.	4·3	12·85	19·1	24·8	4·5	9·0	14·5	20·2	24·25	4·5	9·0	14·6
,, ,, net lb.	1·2	9·75	16·0	21·7	1·4	5·9	11·4	17·1	21·15	1·4	5·9	11·5
,, ,, torque, lb. ft.	12·9	104·8	172	233·5	15·05	63·5	122·5	184	227	15·05	63·5	123·8
Speed r.p.m...	561·3	513·2	530·1	481·4	620	555·5	536	540·5	482;8	739·5	688	678
Brake Horse Power..	1·38	10·22	17·35	21·4	1·78	6·71	13·0	18·9	20·85	2·12	8·31	15·95
Fuel per B.H.P. hour—lb... ..	4·14	0·99	0·78	0·702	4·16	1·36	0·973	0·804	0·724	4·68	1·425	0·948
Thermal effy. per cent.	3·01	12·5	16·0	17·7	3·0	9·15	12·8	15·5	17·2	2·66	8·74	13·1
Cooling loss B.Th.U. per B.H.P. hr.	43,475	7·975	6·160	5,385	41,430	12,150	7,450	5,880	5,670	38,100	11,540	7,240
Cooling loss per cent.	51·3	39·4	38·7	37·6	48·7	43·6	37·4	35·7	38·3	39·8	39·5	37·3
Ignition	M	M	M	M	M	M	M	M	M	M	M	M
Throttle—in.	$2\frac{1}{2}$	$2\frac{1}{2}$	$2\frac{1}{2}$	$2\frac{7}{16}$	$2\frac{1}{2}$	$2\frac{1}{2}$	$2\frac{1}{2}$	$2\frac{1}{2}$	$2\frac{1}{2}$	$2\frac{1}{2}$	$2\frac{1}{2}$	$2\frac{1}{2}$
Air regulator—in.	$1\frac{1}{16}$	1	1	$\frac{15}{16}$	$\frac{3}{4}$	$\frac{3}{4}$	$\frac{3}{4}$	$\frac{3}{4}$	$\frac{3}{4}$	$\frac{3}{4}$	$\frac{3}{4}$	$\frac{3}{4}$
Barometer—in....	29·72	29·72	29·72	29·72	29·78	29·78	29·78	29·78	29·78	29·93	29·93	29·93
Exhaust, radiation, etc., per cent.	45·7	48·1	45·3	44·7	48·3	47·25	49·8	48·8	44·5	57·54	51·76	49·6

TEST NO.	19.	20.	10.	11.	12.	13.	14.	5.	6.	7.	8.	9.
Nominal speed r.p.m. (approx.) ..	650	650	750	750	750	750	750	900	900	900	900	900
Air Temp. deg. F.	83	84·5	85	84	86	86	87	75	78	81	83	85
Exhaust Temp. deg. F.	1,090	1,125	820	945	1,120	1,230	1,230	960	1,035	1,205	1,280	1,280
Fuel per hour, lb.	17·15	19·1	10·7	13·7	17·3	20·2	25·2	11·3	14·3	17·25	20·7	27·2
Cooling water per hour, lb. ..	1,042	1,051	755	846	1,008	1,180	1,317	816	904	1,120	1,228	1,460
,, ,, Inlet Temp. deg. F.	47·8	47·6	49·1	49·0	48·1	47·5	47	47·3	47·4	47·0	47·4	46·7
,, ,, Outlet Temp. deg. F.	173·7	179·2	170	176·9	172·3	171	167	169.9	173·2	172·5	177·2	168·2
,, ,, Temp. rise deg. F...	125·9	131·6	120·9	127·9	124·2	123·5	120	122·6	125·8	125·5	129·8	121·5
,, ,, B.Th.U. per hour ..	131,190	138,310	91,280	108,200	125,190	145,730	158,040	100,050	113,720	140,560	159,390	177,390
Brake load, gross lb.	19·4	22·7	4·7	9·5	14·5	20·0	25·8	4·5	9·0	14·2	19·3	26·8
,, ,, net lb.	16·3	19·6	1·6	6·4	11·4	16·9	22·7	1·4	5·9	11·1	16·2	23·7
,, ,, torque, lb. ft.	175	211	17·2	68·8	122·8	182	244	15·05	63·5	109·2	174	255
Speed r.p.m...	654	649	787·4	784	757	749	728	901	862	835·7	822·6	784
Brake Horse Power..	21·8	26·3	2·57	10·3	17·6	25·9	33·8	2·58	10·4	19·0	27·2	38·0
Fuel per B.H.P. hour—lb... ..	0·788	0·726	4·17	1·33	0·984	0·78	0·746	4·38	1·375	0·905	0·762	0·716
Thermal effy. per cent.	15·8	17·1	3·0	9·4	12·7	16·0	16·7	2·84	9·0	13·8	16·3	17·4
Cooling loss B.Th.U. per B.H.P. hr.	6,020	5,260	35,520	10,500	7,110	5,630	4,680	38,780	10,940	7,400	5,860	4,670
Cooling loss per cent.	37·4	35·4	41·8	38·7	35·4	35·2	30·7	43·3	38·9	39·8	37·6	31·9
Ignition	M	M	M	M	M	M	M	M	M	M	M	M
Throttle—in.	2½	2½	2½	2½	2½	2½	2½	2¾	2¾	2¾	2¾	2¾
Air regulator—in.	¾	¾	¾	¾	¾	¾	¾	¾	¾	¾	¾	¾
Barometer—in.	29·93	29·93	30·18	30·18	30·18	30·18	30·18	30·23	30·23	30·23	30·23	30·23
Exhaust, radiation, etc., per cent.	46·8	47·5	55·2	51·9	51·9	48·8	52·6	53·86	52·1	46·4	46·1	50·7

Test results on Climax model K engine.

improvement in performance due to better lubrication. The engine ran much more smoothly, however, under these conditions.

The curves in Figs. 3 to 8 and 11 were plotted from the actual test results, but those in Figs. 9 and 10 were drawn by selecting constant values of brake horse-power and plotting the corresponding speeds,

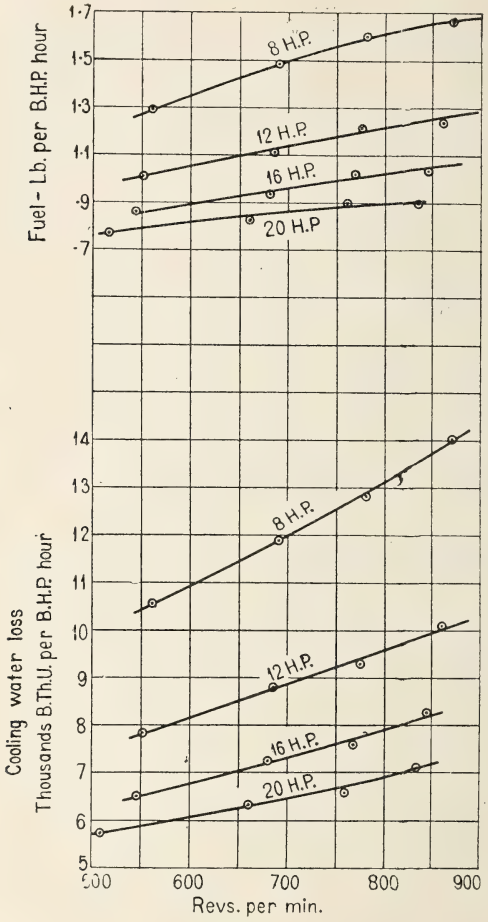


FIG. 9.

cooling losses, fuel consumptions, and exhaust temperatures for each of these values. In this way the influence of speed upon these conditions was deduced.

The thermal efficiencies (brake) plotted in Fig. 11 were based upon an experimental determination of the calorific value of the petrol used, made by Prof. L. J. Rogers, of the University of Toronto.

In Fig. 3 is illustrated the manner in which the exhaust temperature

rises with increasing powers at the various settings of the governor spring. The temperature corresponding to no-load conditions at 900 r.p.m. is about 930° F., and with rising power the exhaust temperature increases at a nearly constant rate up to about half load. Beyond this point the curves bend over until the temperature becomes practically

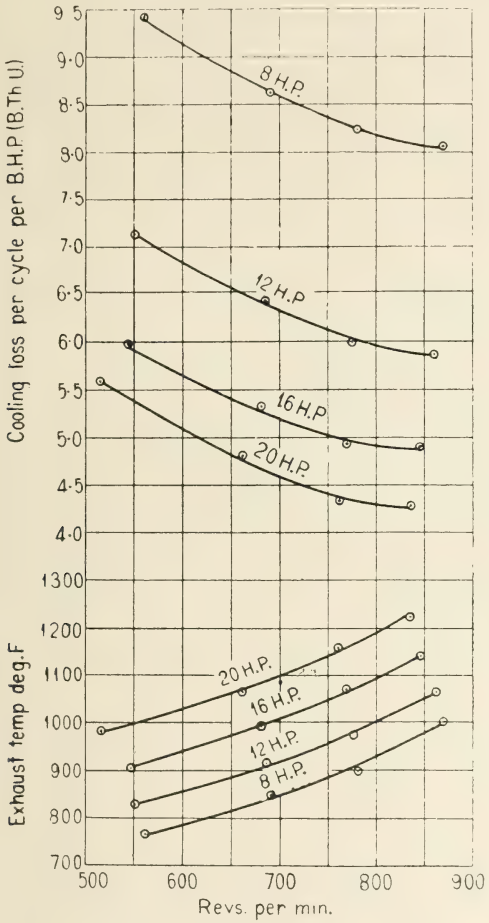


FIG. 10.

constant. This flattening out tendency is less marked at the lower speeds with their smaller power capacities.

The tabulated figures show that in tests 16 to 20, 10 to 14, and 5 to 9, the loss of heat to the cooling water, expressed as a percentage of the total heat supplied to the engine, becomes less as the horse-power increases, the combined losses due to radiation and exhaust gas increasing considerably at high powers in spite of the greater thermal efficiencies obtained.

The curves given in Fig. 3, however, do not represent changes of exhaust temperature at constant speed. The fall of engine speed with increasing loads is shown graphically in Fig. 4, the actual speeds being given in the table of test results. Various powers were, therefore, chosen arbitrarily, the corresponding speeds and exhaust temperatures obtained from the curves in Figs. 3 and 4, and the results plotted in Fig. 10. The loads selected for this purpose were 20, 16, 12, and 8 brake horse-power respectively, so that each of the curves in Fig. 10 corresponds to one of these powers. The curves thus drawn are nearly straight, and are approximately parallel to one another, indicating that, with constant loading, a given increase of speed is accompanied by a definite rise of exhaust temperature, and that the rate of increase is independent of the particular power selected.

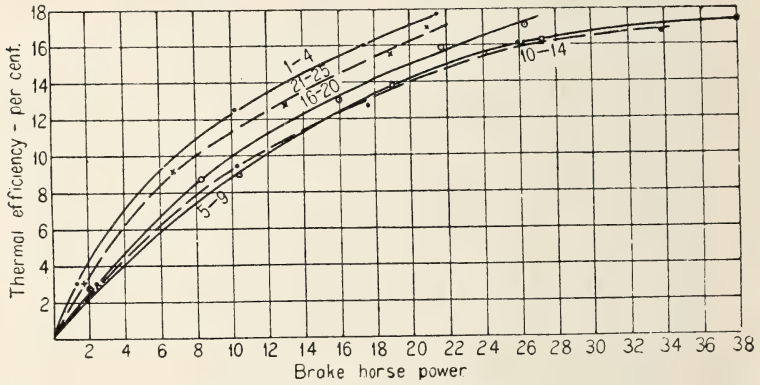


FIG. 11.—Brake thermal efficiencies.

The weight of petrol consumed per hour at different loads is shown in Fig. 5. These fuel consumption curves are nearly straight, but have a distinct tendency to curve upward at powers exceeding 26 b.h.p. The probable no-load consumption is found by extending these curves to meet the zero ordinate. Thus the no-load fuel consumption for series 21 to 25 is 6.5 lb. per hour, and that for series 5 to 9 is 10.3 lb. per hour. The greater mechanical losses at the higher speed involve an extra petrol consumption of about 60 per cent.

Consumptions of petrol per b.h.p. hour are given in Fig. 6, and it will be seen that the low-speed curves lie consistently below those at higher speeds, but that the curves tend to merge into one another as the speed rises to the maximum. The consumption curves for the 5 to 9 and 10 to 14 series are very nearly coincident.

These facts are again illustrated by Fig. 11, in which the thermal efficiencies calculated from the fuel consumptions and brake horse-

powers are plotted. Throughout these tests petrol having a specific gravity of 0.7159 at 67° F. was used, the higher calorific value being 20,450 B.Th.U. per lb. As the minimum fuel consumption was 0.716 lb. per b.h.p. hour, the best thermal efficiency obtained on this engine (apart from tests 1 to 4) was 17.4 per cent. The efficiency of the air standard (constant volume) cycle corresponding to a compression ratio of 3.6 is 40.1 per cent., and therefore the maximum efficiency ratio on the air standard cycle is 43.5 per cent.

The substitution of thicker oil in the crank case (previously mentioned) resulted in an increase of petrol consumption from 0.702 in test 4, to 0.724 lb. per b.h.p. hour in test 25, and a reduction of thermal efficiency from 17.7 to 17.2 per cent.

A further analysis of fuel consumptions is contained in Fig. 9. Curves of constant horse-power were drawn in a similar manner to those already described in connection with exhaust temperatures, but in this case fuel consumptions in lb. per b.h.p. hour were plotted against speeds. From these it is evident that the fuel consumption increases nearly linearly with the speed, and that the rate of increase becomes greater as the power decreases.

The loss of heat to the cooling water (in B.Th.U. per hour) is shown diagrammatically in Fig. 7. As in the case of the exhaust temperatures, these curves bend over somewhat at all speeds when approaching full load. The percentage of total heat lost to the cooling water drops from 38 at low speeds (test 25) to 31 at high speeds (tests 14 and 9).

At very light loads and low speeds (tests 2 and 21) approximately half the heat in the fuel supplied is absorbed by the cooling water. These losses are again shown in Fig. 8, where the cooling water loss is expressed in B.Th.U. per b.h.p. hour. The curves for low speeds fall consistently below those at higher speeds, but the spaces between the curves tend to diminish as the speed rises, the last two curves being very close together.

The influence of speed on cooling water losses is indicated more clearly in Figs. 9 and 10. The former shows the increased loss per b.h.p. hour which results from a rise in speed, the curves being nearly straight and increasing in steepness as the power is reduced. Fig. 10 indicates that if the cooling water loss per b.h.p. hour is divided by the number of cycles per minute, the result is a series of parallel curves at different powers. A similar series may be drawn for the cooling loss in B.Th.U. per cycle, when another set of parallel curves is obtained, and if equal intervals of power be selected (*e.g.*, 8, 12, 16, etc.), an approximately even spacing is obtained.

THE EFFECT OF AIR ON CUPELLATION LOSSES

By J. T. King, *Assistant Professor of Mining Engineering.*

Foreword

General Outline of the Investigation

This paper is the result of an investigation extending over several years on the effect of air on the cupellation losses which occur in Assaying. The research was carried on in the Assaying Laboratories of the Department of Mining Engineering of the University of Toronto.

Silver only was studied because this gives more serious losses, and because it was believed the information obtained would apply also to gold, on which the losses are less serious at ordinary and usual temperatures. No distinction is here made between absorption and volatilization losses; this has been considered worthy of special study. The information to be given has been divided into Parts I, II, III, IV and V.

Part I deals with the difficulties of research on this subject, with temperatures of cupellation, and with references in the literature to air supply.

In Part II those studies relating to the effect of volume and method of application of air are described, also experiments using oxygen and nitrogen. The results of muffle draft tests on gas and coal furnaces are given, as well as practical tests in these to illustrate the effect of various air supplies under actual working conditions.

In Part III will be found the relation obtained between loss and air temperature; with constant air supply the loss here was found to increase directly with air temperature. A résumé is given of various phenomena observed in the foregoing work, pertaining to opening temperatures, frozen buttons, lead in beads and other co-related conditions.

Part IV relates to a study of the effects on loss of amount of lead present, and of amount of silver present.

In Part V temperatures of the surface litharge on the cupelling alloy were taken throughout, to show the relation between this and loss, under varying air supplies. The high rate of loss at the end of cupellation was investigated.

The large amount of work done will be understood, when it is stated that over three thousand cupellations were performed; many of these run in pairs and singly. Some phases of the subject investigated, not described here, may be the subject of further papers.

In the experimental work, assistance was given by Mr. R. J. Henry, B.A.Sc., then a fourth year student, some four years ago, the succeeding year by Mr. C. W. Coo, M.A.Sc. the next year by Mr. Henry and this year by Mr. Coo. The early work was of a general nature with crude apparatus, pioneering exploits in the truest sense. Encouraging progress was made, but it was soon realized that special furnaces and careful control were required.

Coo's early work was performed in a No. 661 Fletcher Russell gas furnace. Air entering the muffle was measured and applied to cupellations in many ways. Later a small wire wound electric resistance furnace was constructed to avoid temperature variations existing with the gas furnace, due to fluctuations in pressure and quality of gas, as well as variable natural chimney draft. Here, voltage troubles, at times, made temperature almost as great an unknown as before. Many mechanical features and operations were early standardized, which later proved to be invaluable aids and time savers. Many important principles relating to air were sensed, but due to limitations in the apparatus, the conclusions could not be proved, except in a general manner.

The later work by Henry, Coo, and the writer substantiates many previous conclusions, and provides ample material for their proof. This recent work has been largely performed in a specially designed Hoskins automatically controlled electric muffle furnace,—where temperatures could be controlled closely over extended periods of time. Confirmatory work under service conditions has been done in gas, in coal, and in other electric furnaces by the writer. In this work, assistance was afforded by Mr. C. H. E. Stewart, B.A.Sc., Demonstrator in Mining Engineering, who performed many of the mechanical details.

PART I

The separation of precious metals from lead and other base metals by cupellation has probably been practised as an analytical process for over 3000 years. There are many biblical references (a.b.). M. Cordella (c) found, among the ancient slags at Laurion Greece (where the mines were worked as far back as 1000-1200 B.C.), a cupel of earth. It was of similar shape to those of to-day, being 4 c.m. in diameter with a cavity 1 c.m. deep. Rose (c) gives a description of cupellation as practised in King Henry's time, 1154-1189, sufficiently clear to be followed. The assayers were aware that the losses are influenced by

(a) Percy, J.—Metallurgy of Lead, 1870.
(b) Benner, R. C., and Hartman, M. L.—M. & S. P. Vol. 104, 1912, p. 501.
(c) Smith, E. H.—"A History of Assaying". Bul.I.M.M. Jan.-Feb., 1924.

temperature and other factors, and sixteenth century textbooks describe the use of checks.

Investigation on losses have continued ever since; in some cases they have borne a crop of errors and half-truths. To many the field has been worked out, the last word spoken, the matter is a sealed book. Some having a superficial acquaintance with the subject, view it as a very simple elementary operation, easily understood and performed; those who best understand the opportunities for error appreciate most the difficulty of obtaining check results. Unfortunately, in some quarters the attitude towards silver cupellations is to "let them rip"; numbers of assays per day count. There are those who agree with Rose (d) that: "The aim in an assay should be to get accuate results, not to save time". To all these this article should be of interest.

Kauffman (e) in reviewing his work on silver losses states:—

"A careful study of these results shows some rather large variations in losses, even when the conditions of cupellation are apparently the same". "Small differences that cannot be detected by the eye cause surprising differences in results". Dewey (f) after studying the results of some 10,000 assays gave a warning, which may in brief be summarized:—

(1) Liability to draw wrong conclusions from insufficient data, and offer isolated illustrations to prove general rules.

(2) Difficulty of carrying on several sets of cupellations under even approximately the same conditions.

(3) Minor disturbing factors, often beyond control, may nullify the effect of chief factors, yielding confusing contradictory results, due to the practical difficulty of arranging and controlling the contradictory and intermediate conditions.

Early writers advised low temperature cupellations, and noting that these were accompanied by feathers, would imply air control by them whether wittingly or not. Draught, dampers, and doors were operated, to urge the fire or to cool the muffle as seemed expedient. Naturally many assayers, without appreciating the detrimental effects of wrong methods of application of air to the cupelling lead, did good work, guided by an intuition born of experience.

The opinions cited on air control in the various textbooks on Assaying vary greatly. Some advise high air currents, others low; some almost neglect mention of air. The information is in general confusing; this is probably because no researches have been published dealing speci-

(d) Rose, T. K.—E. & M. J. Vol. 80, Nov. 18, 1905.
(e) Kauffman, W. H.—E. & M. J. Vol. 80, Nov. 18, 1905.
(f) Dewey, F. P.—Bone Ash Cupels. T.A.I.M.E. Vol. 159, 1918.

fically with the question. The published cupellation losses disagree among themselves, and between the work of different investigators. This is in part due to the fact that no two operators have the same method of defining temperatures; there is as yet no recognized standard of comparison. In the descriptions accompanying the various tables consulted, no mention is made of air control, save that the experiments were carried out under feather conditions, or some similar general statement. Some of the disagreement which exists is undoubtedly due to lack of air control. To obtain some of the agreement shown, close air control must have been used.

The classic experiments of Fulton (g) (h) in 1908, relating to temperatures of opening, freezing, feathers and surfusion, as well as of air and lead, have done much to clear our vision. His work was performed in cupels over 3″ in diameter, with large amounts of lead. He defined the various temperatures for his work. He says:—"It is just as essential to regulate the air draft of the muffle as its temperature," and further, "where very accurate cupellation work is required, such as in bullion assaying, and where the amount of work justifies it, a furnace designed for close temperature and air control is practically essential."

Smith (i) says:—"The regulation of the amount of air passing into the muffle during cupellation is of considerable importance, and is a matter which does not always receive sufficient attention," and later, "the discrepancies between the different observations of muffle temperatures are due, among other causes, to the variation of the air current passing through the muffle, and to the fact that the temperature of the air above the cupel cannot be taken by a thermocouple on account of the radiation of heat from the cupel and from the walls of the muffle."

Dewey (j) considers, "the temperature of cupellation," that of the lead alloy, as the most troublesome variable in assaying, the most difficult condition to control and duplicate, probably the most potent factor in its effect in cupel absorption. It controls the results and success of a cupellation, and is entirely different from any pyrometer reading that can be obtained in practical work, such as air temperature. He says: "Probably the chief cause of variation between the two temperatures lies in the amount of oxygen supplied to the cupelling bead, which is influenced both by the natural draft conditions of the muffle and the freedom with which air is allowed to enter the muffle." He then

(g) Chas. Fulton—E. & M. J. Vol. 86, 1908.
(h) and Manual of Fire Assaying, 1911.
(i) Smith, E. C.—The Sampling and Assay of the Precious Metals, 1913.
(j) loc.cit.—p. 209.

illustrates how the opening and closing of the muffle door may give very erroneous comparative conditions between the air temperature as indicated and the actual bead temperature, *i.e.*, the reading may be falling, while the lead temperature really is rising.

The foregoing are among the outstanding statements relative to air supply, and afford a proper warning to any investigator. It seemed evident that it would be futile, while studying the effect of air supply, to operate the muffle door in and out as in ordinary practice. Air temperatures are instantly changed by moving the door, due to changes in the amount of cold air admitted and in its direction and velocity of flow, as well as to the heat losses at the door. Approximate comparisons in successive runs could be made, if the door was operated in and out in the same manner in each run, *i.e.*, at and for the same length of time and following the same exact cycles of position. Even then, under ordinary chimney draft, which varies largely, as will be shown, the amount of air passing through the muffle would change, with its consequent effect on all temperatures, viz.: of the air, the alloy, the cupel and the muffle.

Much of this investigation was carried on using a closed muffle door throughout and known air supplies, to avoid the aforementioned troubles. Many precautions and much care was taken to standardize procedure, so that experiments could be duplicated, some of which it is hoped will be new to the reader. These are described as they occur.

PART II

APPARATUS AND EXPERIMENTAL CONDITIONS

The Furnace.

Fig. 1 shows the Hoskins F.B. Electric Resistance Furnace, with automatic control. The muffle of crystolon is 19″ long, 12″ wide and 8″ high, and has a nichrome alloy tray. The 14 nichrome heating elements are of hairpin type. Fumes are exhausted by fan suction when required.

Current at 110 volts a.c. is reduced at the transformer to either 45 or 37 volts. On 45 volts the temperature would exceed the safe limit of 1100° C. in two hours; with 37 volts a maximum of about 950° C. was obtainable, operating with a closed door. Either hand or automatic control may be used at either voltage.

A chromel-alumel couple in the muffle is connected with the indicator of the control, where the muffle temperature changes are shown by the usual movement of a pointer over a scale. A second pointer or boom, operated by hand, is set to the temperature at which it is desired to

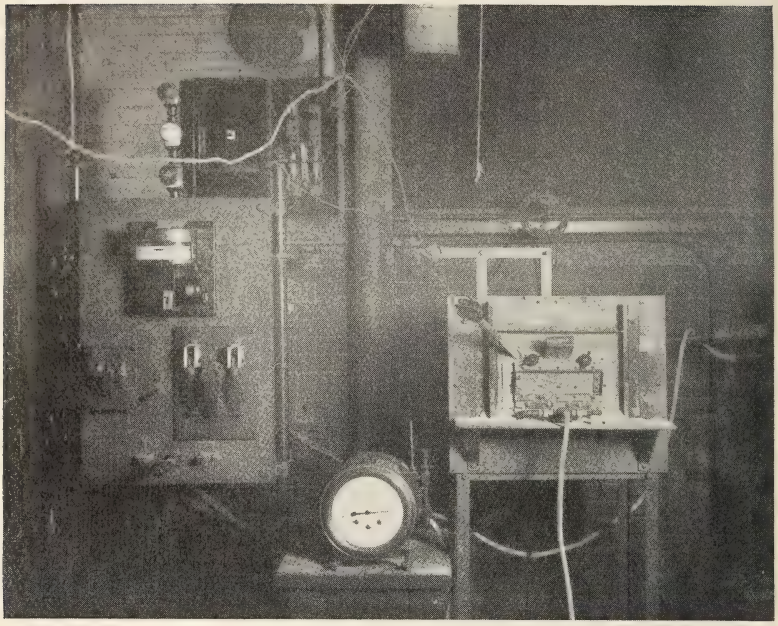
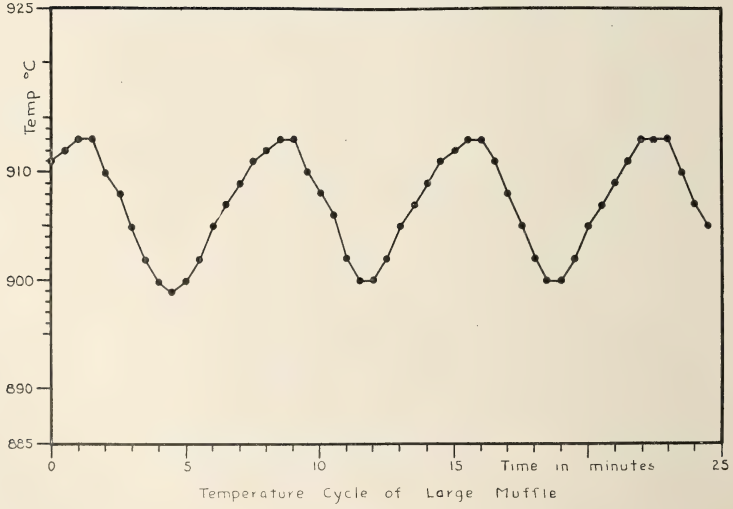


Fig. 1.



Temperature Cycle of Large Muffle

Curve 1.

operate. The boom has three contacts, connected with three signal lamps, and with a relay, which actuates the main power switch of magnetic type. A motor and cam actuate a vertical pin at 20 second periods. The pin depresses the boom, and when the moving pointer is below the boom, the pointer raises whichever contact it meets. The position of the contact, whether up or down, is indicated by the lights. Only two adjacent contacts may be up or down at once; this gives five combinations of power conditions, thus:—

LIGHTS		
RED	WHITE	BLUE
On	Off	Off
On	On	Off
Off	On	Off
Off	On	On
Off	Off	On

Power is on only when the red light is on. Power was applied when the temperature dropped about 6° C. below the boom setting; this was followed by a further drop of about 3° C. with power applied, before the temperature began to rise. On the rise, power was cut off; when the moving pointer was about 2° C. above the boom setting, the temperature rose 1 or 2° more with power off. Thus, generally speaking, the maximum range of temperature variation was from 10 to 12° C. The first boom supplied did not hold within these limits after some months' use, probably due to severe wear on the contact pins, operating at a fixed position. When replaced by an improved boom, but little further variation in range was experienced. Curve 1 shows a typical rise and fall cycle of temperature at a setting of 910° C. with 6 litres of air per minute passing through the muffle.

Cupels of Bone Ash.

The bone ash used in most of the experiments was from one shipment. Several boxes were mixed thoroughly after drying. A sample of 400 grams was selected by a Jones riffle, and again dried. This was screened for eighteen minutes in an automatic machine having 240 bumps to the minute, and gave this analysis with Tyler screens:—

SCREEN	PERCENTAGE
+ 28	0
35	0.02
48	0.03
65	1.02
100	24.90
150	27.18
200	24.85
300	15.85
— 300	6.15

An Ihler type foot cupel machine was used. The mould diameter was 1¼", and depth of cup 7/32". To the foot was attached a wooden extension 4 feet in length; on the extremity of this a box was placed in a fixed position. Above the box on a stand a large funnel was held. The apparatus is shown in Fig. 2. Into the funnel 55 lbs. of granulated lead was poured. The lead stream falling into the box applied a steadily increasing pressure on the lever, reaching to a maximum when all had fallen, in about one minute. The pressure to a square inch of cupel surface was 800 pounds. As a basis of comparison it may be stated that a 200 lb. man standing on the pedal of the machine would exert a pressure of 525 lbs. to the square inch of cupel surface. It is

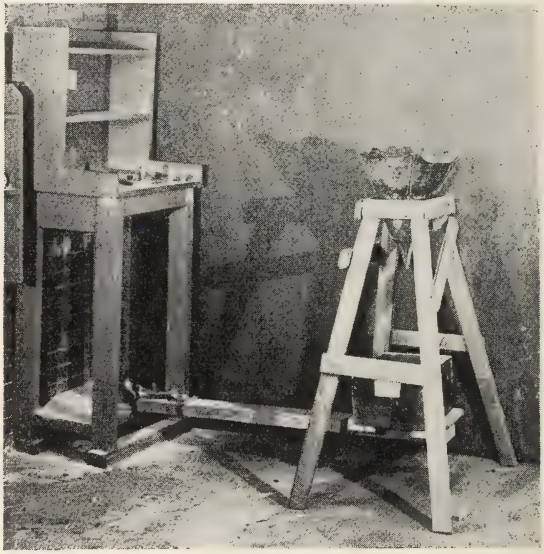


Fig. 2.

seen, then, that the cupels made with the falling lead were firmer than is usual, though operators often increase the effect of their weight on the pedal by a downward motion of the body. A mix of 33 grams per cupel was used, 90% of ash and 10% of water. This gave cupels one inch in height. Small batches at a time were made up, and cupel portions were weighed while the lead was falling. This procedure was adopted to avoid different moisture content in the cupels which occurs, due to evaporation, if large amounts are mixed ahead. While the process was not fast, it did give what was desired, cupels of indisputable similarity as to height, pressure, moisture and weight. These were aged for months before being used, though this was not really neces-

sary. It was fortunate that a large stock of this ash was on hand, because many tests performed on cupels using a different lot of the same grade of ash from the same source showed a difference of 0.08% in loss. This latter ash gave a different screen analysis, and packed more closely than the former.

Sheet Lead and Standard Buttons.

For the synthetic buttons, sheet lead, all of one shipment, was used. Samples were selected from each of the rolls and were found to contain 0.02 ounces of silver per ton. Fifteen grams of lead weighed to within 0.1 gram were used for each button. The silver was wrapped in this amount of lead, then the rough, irregular, loosely wrapped packet was compressed in a metal mould under a standard load to give a hard smooth surfaced button of cylindrical form 19/32 inch in diameter and ¼ inch in thickness. With this standardized procedure the time required to open the buttons under other constant conditions was very uniform. They opened at about 10° C. lower temperature than loosely compressed ones, and more quickly. The correction for silver of 0.01 milligram per 15 grams of lead was neglected save in those experiments, where the loss on 1 and 5 milligrams of silver present was determined.

Silver.

For practically all of the experiments, silver prepared in the laboratory was utilized. Silver purchased as pure was dissolved in nitric acid, allowed to settle, and decanted three times to eliminate insoluble and dirt. Hydrochloric acid was added; the chloride was washed several times with distilled water. After drying, the chloride was fused with sodium carbonate, and the reduced silver was poured into a bar. This bar was electrolysed, as outlined in Scott (k). The feathery crystals were washed, dried, and then melted under a borax cover. The resultant bars were rolled into strips ready for use as required. Towards the completion of the work this silver became exhausted, and was replaced by pure silver from the Philadelphia Mint. Various tests of these silvers, by cupellation and the humid method, showed them to be of equal purity. Unless otherwise stated, all the buttons contained between 100 and 101 milligrams of silver.

The Twin Muffle.

Before the furnace was in operation there was some doubt as to whether it would really duplicate temperatures on successive runs,

(k) Scott, W. W.—"Technical Analysis."

using the same setting of the boom. Whether a cupellation was started on the peak, or in the trough of a temperature cycle, as well as mechanical defects in the contact pins, would contribute to variations of several degrees. It was found that the furnace was a few degrees hotter at the centre of the muffle than at either front or back. There was a gross variation across the central line of the muffle of 7° C. These differences were fairly constant for any one fixed position of the base metal couple for muffle control, but when the position was altered the gross variations changed. After some trials with different positions, it was decided to place the control couple about one inch from the muffle floor, and just behind the central line. With a closed muffle and the furnace body saturated with heat, using this location, the regulator responded quickly, and reduced the temperature changes to a minimum.

Equality in comparative measurements is an ideal to strive for, but which is seldom attained. By what standard should we measure either equality or inequality in cupellation? What was to be our yard stick? Could two cupellations be dependable in each test, one run under constant conditions, always giving the same loss and known aa a standard; the other to have a variable air condition, but otherwise under the same conditions as the standard? No method of doing this in a single muffle was conceived. Any variation of air supply to one cupel would, obviously, affect the others. Nor could we conceive how strict comparisons could be made on a basis of air supply if the muffle door was open. The time-honoured custom of opening a button is with the doors closed; when the uncovering occurs, the door is opened, more or less, as is the assayer's custom. This introduces temperature changes in the muffle depending on many things; it is practically impossible to run a series of cupellations in this manner and obtain comparable results, simply because we cannot exactly duplicate conditions run after run.

The solution of the difficulty seemed to lie in having two small muffles as identical in every respect as it was possible to obtain them, and placed beside each other in the large or furnace muffle. In one would be run the standard cupellation under constant air supply; in the other the corresponding cupellation with a varied air supply. Any departure from the usual loss in the standard muffle would indicate the possibility of an altered furnace temperature condition, and even though the cause was not known, would be a signal to discard the result from the variable muffle. It was found later, that while using a well diffused air supply of low volume, 0.2 cubic feet per minute, a change of 1° C. in air temperature caused a change in loss of 0.015%. Scanning the

early tables and curves in this respect will show that a variation of only three or four degrees is sufficient to destroy the consistency of the results obtained.

Construction of the Twin Muffle Door.

In Fig. 1 is shown a special door used in Part III and replacing the usual sliding door supplied with the furnace. In this Part II, the door used is shown in Fig. 3, to which are attached the twin muffles. Figs. 4 and 5 show the essential details of its construction. Fig. 6 shows in diagram the set up of Fig. 1, but with the twin muffle door in place.

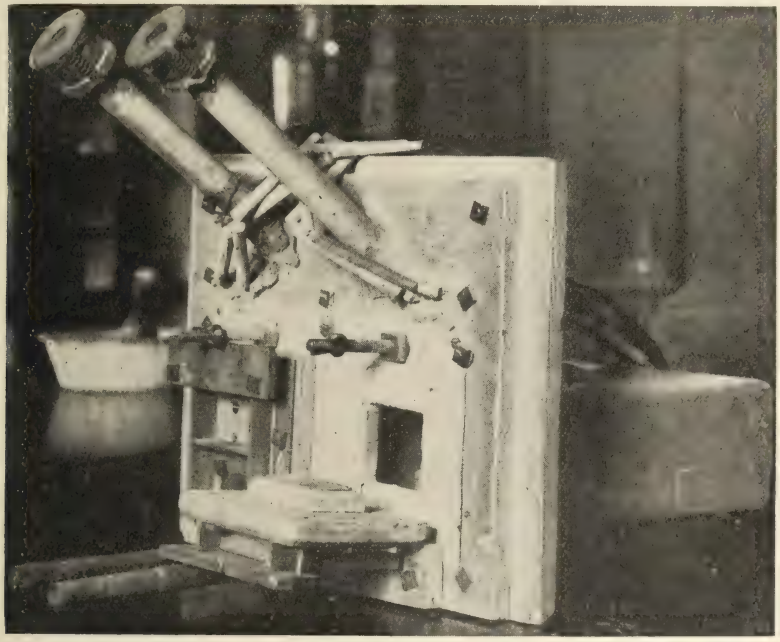


Fig. 3.

The muffles were crystolon; they were closed at the rear end. A round hole 5/8" in diameter for the exit of fumes was placed at the centre. The outside dimensions were 10" in length, 4½" in width, and 3½" in height, the walls being ¼" in thickness. The open ends of these muffles fitted into apertures cut in two adjoining asbestos plates of ½" thickness, and rested against a similar third plate with slightly smaller apertures, these latter being the doorways. The doors D were also of asbestos, hinged at the bottom, and held tightly closed by wing nuts. They were stiffened with ¾" angle iron to prevent warping.

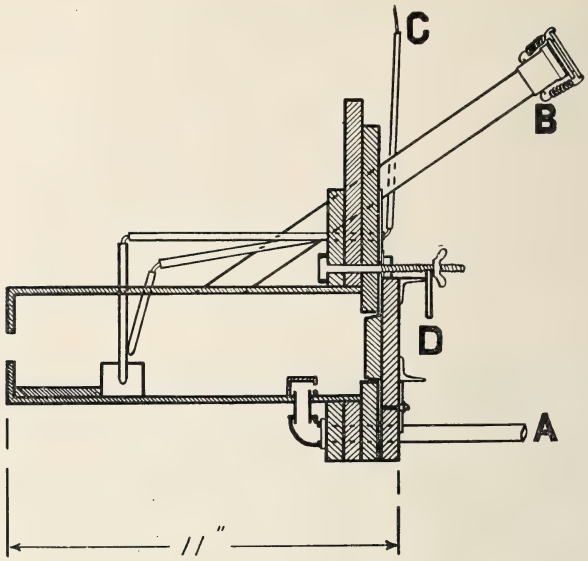


Fig. 4.

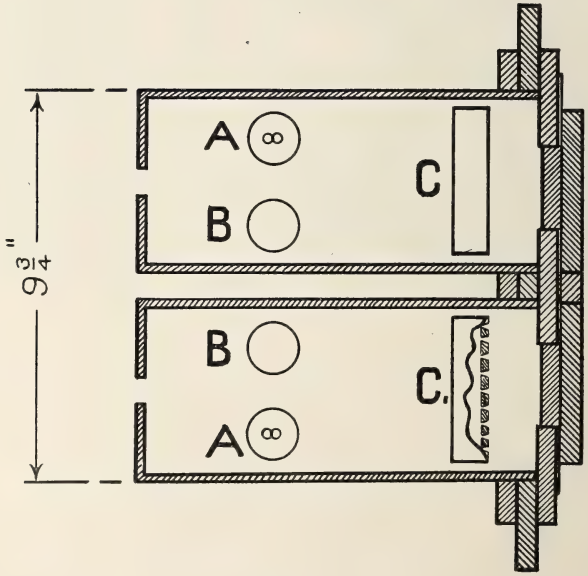


Fig. 5.

Several sheets of soft asbestos paper acted as packing between the doors and the plate on which they closed, thus giving a reasonably good air-tight joint. The plates were fastened by bolts. The whole door was placed in the muffle entrance, and was tightly wedged into position. Alundum cement was used to close all joints in the structure. It stood up well, without warping, and few cracks developed. These were filled when observed, with cement.

Observation Tubes.

B of Fig. 4 is a fire clay tube 7/8" in diameter, fitted at the outer end with a removable glass plate, held in place by springs, against rubber packing. These observation tubes, one to each of the twin muffles, were so directed that the cupelling lead in the muffle could be completely

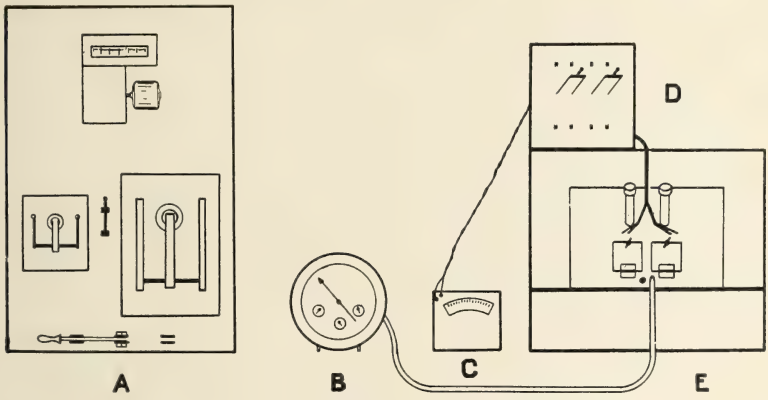


Fig. 6.

observed throughout the most of a cupellation, and the time of cupellation be taken. They were elevated at as high an angle as the large furnace muffle would permit. Optical temperatures of the cupellation could be taken with the Leeds and Northrup instrument used. The tubes are shown, one for each muffle, in Fig. 3.

Air and Blank Cupel Temperatures

A, in both muffles shown in Fig. 5, represents fixed dummy bone ash cupels. Into each was placed a Pt. — Pt. Rd. couple, and also 1/4" above each was a similar couple, these for measuring cupel blank, and air temperatures respectively. Each couple extended outside the furnace to a control board D, and through double-throw switches were connected to a Leeds and Northrup Pyrovolter shown in Fig. 6. The couples within the muffles were strung through clay tubes, these being

covered with alundum cement. They were checked against the melting points of lead, sodium chloride and copper, and compared with a Cambridge Instrument Co. platinum resistance pyrometer of Whipple pattern, as was also the optical pyrometer used to measure the surface temperature.

Measurement of Air.

To each muffle, through a ¼" iron pipe shown at A in Fig. 4, air could be admitted. The pipe of the standard or left muffle was seldom used. Air to the right or variable muffle was measured through a Precision Company laboratory meter shown at B of Fig. 6. The capacity was 0.7 cubic foot per minute. An air diffuser, to direct air in various ways in the muffles, is represented in Fig. 4 over the supply pipe, and at C in Fig. 5. Fig. 6 is a diagrammatic front view of the whole lay-out, showing the control board, air meter, pyrovolter, switches and furnace with the twin muffles and accessories.

The left muffle (referred to as muffle A) was used throughout as the standard. No air was admitted at the supply pipe. The door was closed tightly; the cupellation was carried on by that air already in the muffle, augmented by that which leaked in through any cracks, and the exit vent at the rear. Cupellations in this, with 15 grams of lead, required 25 minutes for completion. The air supply here was very low, and practically constant, no matter how much was supplied to the right hand or B muffle. Air to this was forced through the Precision meter and measured. This meter was checked by the displacement of air by water from vessels of known volume. A suction amounting to 2.0 cubic feet per minute, with the doors open, was maintained at the rear of the large furnace muffle. This prevented a back pressure into the A muffle, which otherwise occurred, and allowed it to vary slightly in the same direction as the B muffle loss, especially when the higher air supplies were used in the latter. The main air supply was from a gasometer tank of about 1000 gallons capacity, which gave a very constant pressure.

Temperatures of Furnace Muffle.

The boom of the control was fixed at 920° C. and was not altered during the experiments. This gave an average cupel temperature in the A muffle of 916° C. and in the B muffle of 910° C. In curve No. 1 is shown a graph of the large muffle temperature variations over the period of a cupellation using a boom setting of 910° C. The blank cupellation temperatures in the twin muffles usually sympathized only a degree or two with the rise and fall shown in the large muffle,

and did not always follow a similar cycle. This was because the twin muffle walls served as a heat reservoir; and, being midway between the large muffle floor and roof, received more radiated heat from the roof than did the large muffle thermocouple located nearer the floor.

Time.

The time of cupellation recorded is the total time elapsing between the opening of a button, and the first play of colors. Buttons were always placed in the cupels immediately after the power was cut off, while the temperature was still rising, so that they would open on a peak of the temperature cycle. The time was taken with a seconds stop watch, but, in as much as it was difficult to locate the beginning and end of the cupellation exactly, these time readings are recorded to the nearest quarter minute.

Weighing.

Silver for the buttons and the resulting beads were weighed on a Wilfred Heusser bead balance. This was sensitive to less than 0.005 milligram. With a balance load of 100 milligrams an addition of 0.005 milligram to one side gave a real appreciable pointer movement. Beads were weighed to 0.01 milligram; the same 100 milligram weight was used in all weighings. Each button consisted of 15 grams of lead to within 0.1 gram, and between 100 and 101 milligrams of silver, unless otherwise stated.

Correction and Discarding of Results.

Those results where the standard or left hand muffle cupellation gave a loss of 0.15% higher or lower than the average were discarded as untrustworthy. This average loss was established from sixty experiments to be 2.24%. The remaining results were corrected by that amount plus or minus, which the standard varied from 2.24%, within the limits stated. For example, the loss on the standard was 2.26% and on the variable 2.42%. The standard was 0.02% high; this correction applied to the variable gave 2.40%. These corrected results are the ones recorded in the tables to follow. This adjustment was justifiable, because it was known that the temperature varied slightly. When the standard through any cause gained or lost, it was fair to assume that the variable was similarly affected. Since the results were plotted on the basis of one temperature, these corrections were necessary.

The above method of interpreting the results was adopted because no consistent relation between either blank cupel or air temperatures and loss could be found with the cupels placed as they were here, to

one side of the actual cupellation. Failing in this, but few such temperatures were taken in the experiments to be described, except as a check on the constancy of the temperature difference between the A and B muffles, before cupellations. Attention was consequently focussed more on the regularity of the automatic temperature control. Slight variations in the large muffle temperature cycle, from run to run, and in the same run, caused differences in loss in both twin muffles, which was not accounted for by the corresponding change in the blank or air temperatures. These cycle variations resulted partly from variation in the primary voltage, and in the condition of the contacts at the control, at the circuit breaker and at the individual resistance units. The time taken to charge buttons, and the proximity of this period to the peak of the cycle, were important.

EXPERIMENTAL PART. SERIES 1—10.

The experiments to be described here were planned to show, in a way easy of interpretation and application to practice, how the rates at which air is supplied to a muffle affect loss, and how also, the loss is affected by altering the method of applying each rate of air to the muffle.

It should be pointed out that the twin muffles, 10 × 4½ × 3½ inches, have a volume of about 2.6 litres. Taking into account the expansion due to rise in temperature from that of the room at 20° C. to that of the muffle at 910°, it is found that 0.65 litre of the room air is necessary to fill the muffle, assuming that there is no change in pressure. The room air required to supply sufficient oxygen to convert 15 grams of lead to litharge is approximately 4.3 litres. Allowing for that air already in the muffle, there must be supplied at least the difference or 3.65 litres of air during the cupellation to oxydize the lead. Assuming a cupellation period of 18.5 minutes, the average rate of air supply per minute, then, is 0.2 litres. Manifestly, if at any time the oxygen in the muffle is all used, cupellation will cease, but owing to leakage to the standard twin muffle, which could not be overcome with our type of apparatus, this never occurred.

SERIES 1—WELL DIFFUSED AIR SUPPLY.

The set-up for this is shown in plan and elevation in Fig. 7. Air was admitted through the inverted trough, which had 9 holes of ⅛ inch diameter, and facing the door. Little is known of just how the air currents travel. Air emerging from the trough would be deflected upwards by the door, and then towards the rear. This air must have

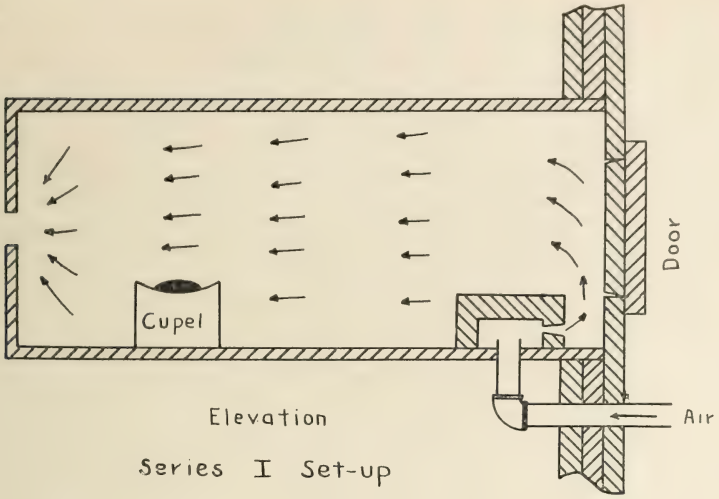
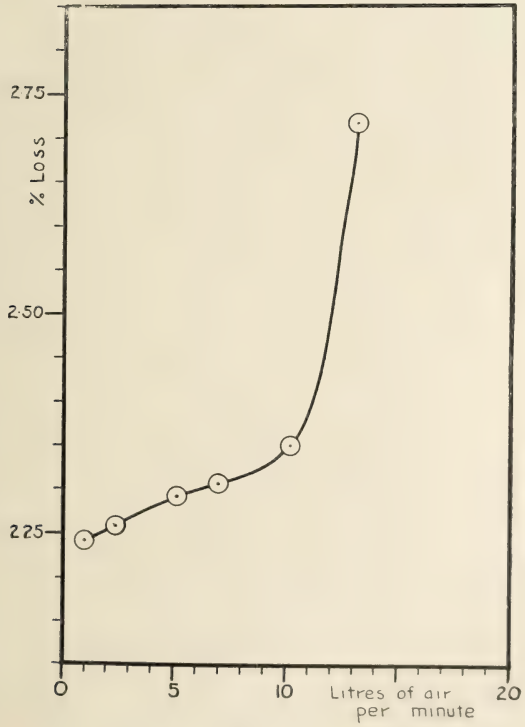

Cupel
Door
Air
Elevation
Series I Set-up

Fig. 7.


2·75
% Loss
2·50
2·25
0
5
10
20
Litres of air per minute

Curve 2.

been well heated surrounding the cupels, because the thermocouple inside the blank cupel showed a drop of only 5° C. at the maximum air rate used here. The cupellation of 15 grams of lead liberates 3675 calories, and although this heat does have its effect in heating the air passing over the cupel, this is greatly surpassed by the heat input to the muffle here. The reaction does not liberate sufficient heat of itself to maintain the ruling temperature necessary for its continuation.

Under this method of diffusion, and the opportunity afforded the air to heat before reaching the cupel, it may be concluded that there would be little tendency for the air to layer out in strata of greatly different temperature due to hydrostatic equilibrium. The air being fairly uniformly heated, eddies would be at a minimum. The cupelling lead would be supplied with air moving over it at much lower velocity for a given rate of supply than in the subsequent series. Attempts to simulate the eddies formed were made by observing the paths of colored vapors passing through a muffle, but once the muffle becomes filled with these, the movements become very complex even at low temperatures. Ammonium chloride vapors, tobacco smoke and other visible fumes were passed through a glass case similar in shape to the muffles, and using many methods of applying the same. Slight changes in temperature quickly alter any established direction of the fumes. Another point may be emphasized, that is, the effect of slight variations in the muffle wall, or of objects placed inside the walls, such as uneven layers of bone ash on the floor, or cupels with their cup shaped tops. These greatly modify and alter the currents of eddies. Hence, in the illustrations here given of paths of air currents through the muffle, the reader will understand that an attempt has been made to illustrate in a very general way a possible explanation of the air paths. These we must conceive in the abstract, as no true visible representation can be made in the present state of our knowledge.

The results of the cupellations appear in Table 1. A group of tests was run on each of several air supplies. The Curve 2 shows the average percentage silver losses plotted against average air rates. Up to 10 litres per minute the loss is almost proportional to the air supplied; the curve is in effect a straight line. Above this amount there is a sharp increase in loss in this set-up. It is likely that eddies or surges form in the air, thus destroying the good diffusion evident at the lower rates. This particular departure from the straight line would be unlikely to hold if tried in another muffle, or for the slightest change of either the trough or cupel positions in this muffle; it is merely a peculiar property of this specific arrangement of relative parts of the muffle. The results are satisfactory, in that there is a general trend of the curve in one

direction, but the loss increase is so small that conclusions here must not be taken as proof of the effect of air supply, rather only as one detail in the mass of evidence to be given.

TABLE No. 1. SERIES 1. TEMPERATURE 910° C. WELL DIFFUSED AIR.

Exp. No.	Time min.	Air litres per min.	Average Air	Loss %	Average Loss %
1	15½	14		2.78	
2	15½	13.6		2.60	
3	15	13.1		2.78	
		40.7	13.6	8.16	2.72
4	20¼	10		2.37	
5	20	10		2.36	
6	20	10		2.36	
7	20	11		2.33	
		41	10.2	9.42	2.35
8	20½	7.2		2.32	
9	21	7.0		2.35	
10	—	7.0		2.27	
11	21¾	6.3		2.28	
12	20¼	7.3		2.34	
13	21	7.3		2.31	
		42.1	7.0	13.87	2.31
14	—	5		2.25	
15	21	5.4		2.25	
16	21¼	4.8		2.26	
17	20	5.2		2.33	
18	20	5.0		2.34	
19	20	5.3		2.32	
		30.7	5.1	13.75	2.29
20	22	2.5		2.23	
21	22	2.5		2.27	
22	23	2.4		2.29	
23	22¼	2.1		2.25	
		9.5	2.4	9.04	2.26
24	23¾	1.0	1.0	2.24	2.24
25	24¾	0.4	0.4	2.25	2.25
26	25	0.2	0.2	2.24	2.24

SERIES 2—PARTLY DIFFUSED AIR SUPPLY.

This series was comparable with the former in every respect, except that the position of the air outlets of the inverted trough was reversed. It was placed with the outlets directly towards the cupels as shown in Fig. 8. The results are given in Table 2, and these are shown plotted in Curve 3. This method gave more irregular losses and less agree-

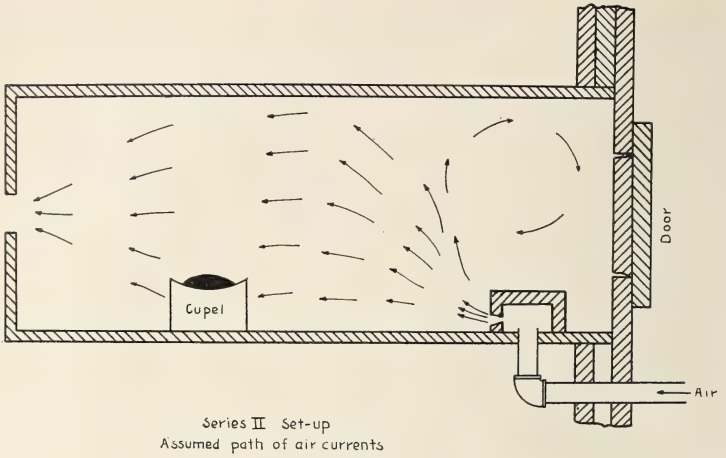
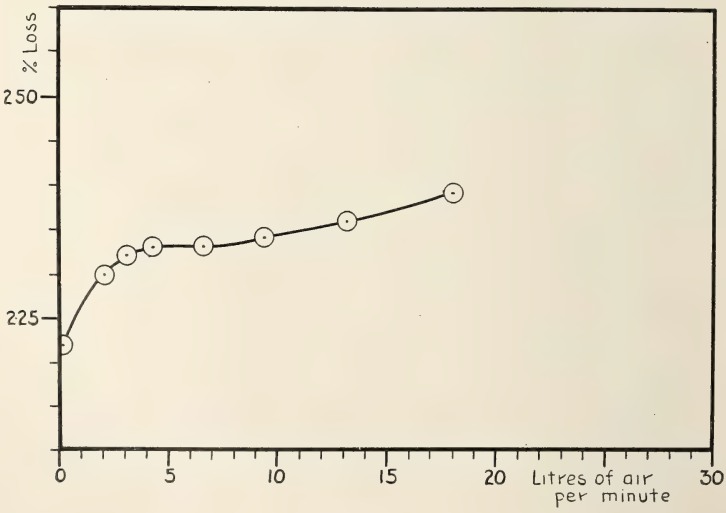


Fig. 8.

ment than Series 1. There was increase in loss with each increase of air. It is evident that for air up to 10 litres per minute, it is almost as well distributed as in the preceding series; larger amounts show still better distribution; the curve does not rise steeply. Higher losses occur at the lower rates than in Series 1; the reverse holds for the higher rates. The distribution of air is quite different from the former series; the condition causing the sharp rise above 10 litres is not present here.



Curve 3.

TABLE NO. 2. SERIES 2. TEMPERATURE 910° C. PARTLY DIFFUSED AIR.

Exp. No.	Time min.	Air litres per min.	Average Air	Loss %	Average Loss %
1	18	18	18.0	2.39	2.39
2	21	13.4			
3	21¼	9.5	13.4	2.36	2.36
4	21½	9.1		2.35	
		18.6		2.33	
5	22	6.6	9.3	4.68	2.34
6	20¾	6.6		2.33	
7	21¾	6.6		2.31	
8	21¾	6.6		2.35	
		26.4		2.33	
9	21¼	4.4	6.6	9.32	2.33
10	21¼	4.3		2.34	
11	21½	4.2		2.35	
				2.30	
		12.9	4.3	6.99	2.33
12	22	3.1		2.33	
13	21¾	3.1		2.30	
14	22	3.1		2.33	
		9.3	3.1	6.96	2.32
15	22¼	2.1		2.30	
16	22½	2.1		2.31	
17	22½	2.1		2.28	
		6.3	2.1	6.89	2.30
18	26	0.2		2.21	
19	26½	0.2		2.23	
		0.4	0.2	4.44	2.22

SERIES 3—A JET OF AIR INDIRECTLY APPLIED.

Here the trough used in Series 1 and 2 was removed, giving conditions as shown in Fig. 9. The results given in Table 3 are plotted in Curve 4. This curve is irregular in that 6 litres of air per minute give lower losses than either less or more air, viz.: 4 litres and 8 litres. Other parts of the curve resemble the previous ones, except that the loss mounts more rapidly. The dip or irregularity for the six litres rate was not due to the cooling effect of air blowing on the cupel, thus giving a lower cupel temperature; the blank cupel temperatures were little affected in this way. This dip may be explained by assuming that certain changes in amounts of air supplied changed the direction of the air currents, thus giving the anomalous condition of less air actually reached the cupellation at the six litre rate. It may be concluded from

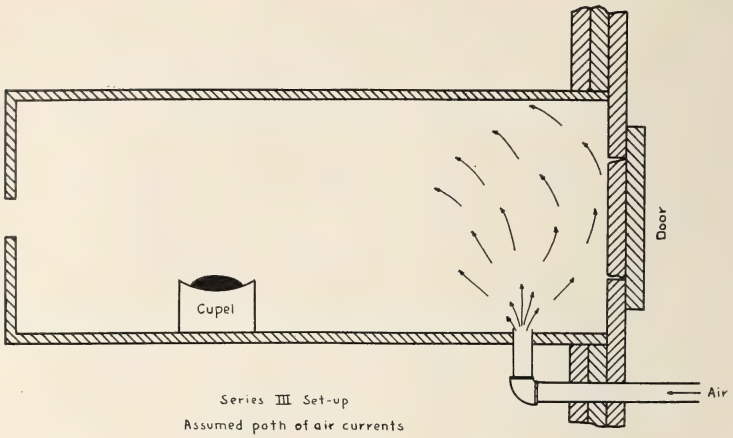
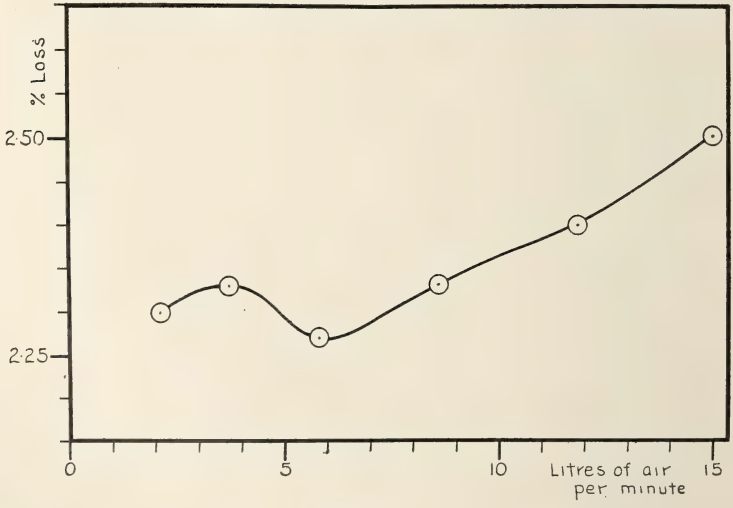


Fig. 9.

the data that the method gives irregular losses, and that passing a small single jet of air into a muffle is bad practice. Such jets cause eddies. If the jet is not directed towards the cupel, the losses may not be unduly large at moderate air supplies, but still of course rise at the higher rates. The practice of using a closed door with one or two round holes in the same, is favourable to high and irregular losses, especially with a high muffle draft. Many muffle doors are thus constructed.



Curve 4.

TABLE NO. 3. SERIES 3. TEMPERATURE 910° C. A JET OF AIR INDIRECTLY APPLIED.

Exp. No.	Time min.	Air litres per min.	Average Air	Loss %	Average Loss %
1	18½	15.0	15.0	2.50	2.50
2	20½	11.7	11.7	2.40	2.40
3	21¼	8.6	8.6	2.33	2.33
4	23	5.8		2.25	
5	23	5.8		2.27	
6	23	5.9		2.28	
Av.	23	17.5	5.8	6.80	2.27
7	22	3.7		2.34	
8	22	3.7		2.32	
Av.	22	7.4	3.7	4.66	2.33
9	22½	2.0		2.29	
10	22¼	2.1		2.31	
11	22¼	2.1		2.31	
Av.	22¼	6.2	2.1	6.91	2.30

SERIES 4—AIR JET DIRECTLY AT CUPEL, FROM A POINT 5 INCHES AWAY.

A 90° elbow was attached to the vertical pipe of Series 3, with the exit pointing at the cupel, the centre of this exit being level with the cupel top. This location is represented in Fig. 10. The increases in losses were quite rapid here, and relatively few cupellations were required to establish the air effect. These results are given in Table 4, and Curve 5 shows the same plotted. It is of especial interest, and worthy of note, that feathers formed only at the higher air rates, where the losses are greatest. These feathers formed as a tight close coherent

TABLE NO. 4. SERIES 4. TEMPERATURE 910° C. JET OF AIR DIRECTLY APPLIED AT 5 INCHES.

Exp. No.	Time min.	Air litres per min.	Average Air.	Loss %	Average Loss %	Remarks
1	11¾	10.0	10	3.41	3.41	Heavy feathers
2	14¾	7	7	2.83	2.83	Light „
3	17	6.3	6.3	2.68	2.68	Very light „
4	17½	5.6	5.6	2.54	2.54	No feathers
5	19¼	4.1		2.41		„ „
6	19¼	4.1		2.44		„ „
Av.	19¼	8.2	4.1	4.85	2.43	„ „
7	22½	2.2		2.33		„ „
8	22½	2.1		2.32		„ „
Av.	22½	4.3	2.1	4.65	2.32	

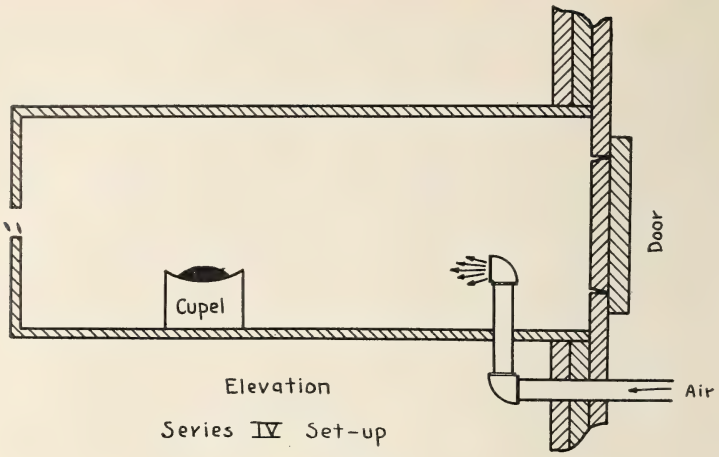
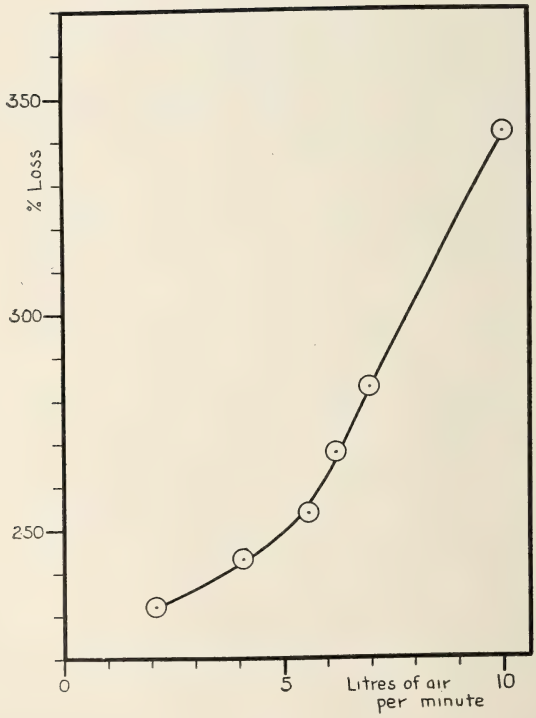


Fig. 10.



Curve 5.

crop, of individual size, about a mm. across. They were much smaller than those occurring at lower temperatures, as in ordinary practice, and with low air supplies. This shows, then, that feather conditions may give quite erroneous impressions relative to loss,—that they do not always indicate a low loss. The loss increase rate for the same air supply is greater here than in the preceding series, hence a direct jet of air aggravates loss.

SERIES 5—AIR JET APPLIED DIRECTLY AT THE CUPEL FROM A DISTANCE OF 1 INCH.

The change here made was to extend the elbow by a pipe of ⅛ inch internal diameter to within one inch of the cupel, as illustrated in Fig. 11. The increase of loss was here so rapid that only a few runs were required to establish the serious losses occurring with this set-up. The information is in Table 5; the relation of loss and air supply is graphically shown in Curve 6. The conditions here are somewhat parallel to Koenig's (1) so-called "Bessemerizing". The lowest air supply caused the surface litharge on the cupelling alloy to appear at nearly white heat. In No. 2, at 9.8 litres per minute, the side of the cupel facing the door was cooled to 770° C. (optical pyrometer), while the temperature of the litharge surface was 1075° C. In No. 1, at 15 litres per minute, which gave a loss of 7.75%, while the lead was in violent ebullition causing a miniature fountain effect, feathers were forming beside the lead, whose surface temperature was 1120° C. towards the end of the cupellation. Feathers formed in spite of the

(1) Koenig, C. A. "Scorification and Cupellation without a Muffle," A.I.M.E. Vol. 28.

Koenig described a furnace, using gasoline torches entering the side walls, opposite to scorifier and cupel positions. The scorifiers and cupels rested on clay supports opposite to the torches. When the desired heat for his cupellation was obtained, *i.e.*, when the lead had melted at a yellow heat, the torches were turned off and replaced by air blasts. Describing a cupellation, he states:—

"The bath looks bright yellow, almost white; it revolves evenly without any oscillation backwards and forwards. The rim of the cupel is dark." He called the process "Bessemerizing."

"The lead fumes pass out of the vent in brown clouds. The lead diminishes in volume, as if it were running through a crack in the cupel." "Thirty grams of lead with ten milligrams of silver have come to the glance in 4½ minutes, and all this time the heat was shut off. This rate of speed, however, is not commendable. Though I have obtained satisfactory results with the high speed, in the general run the silver results are too low." He found the best time for 30 gram buttons to be 7½ minutes.

In our work such fast cupellations under our conditions always gave an abnormally high loss.

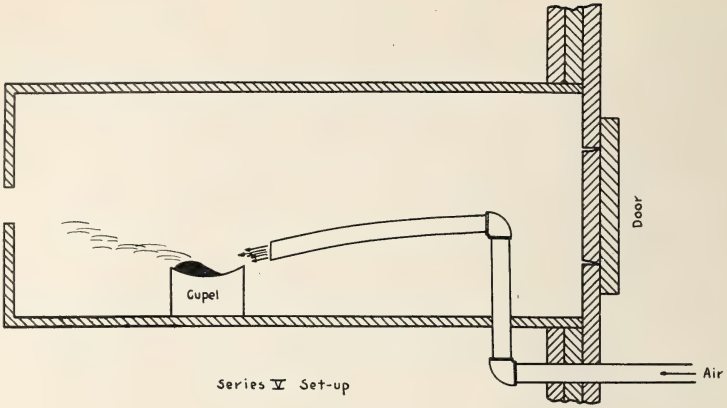


Fig. 11.

Curve 6.

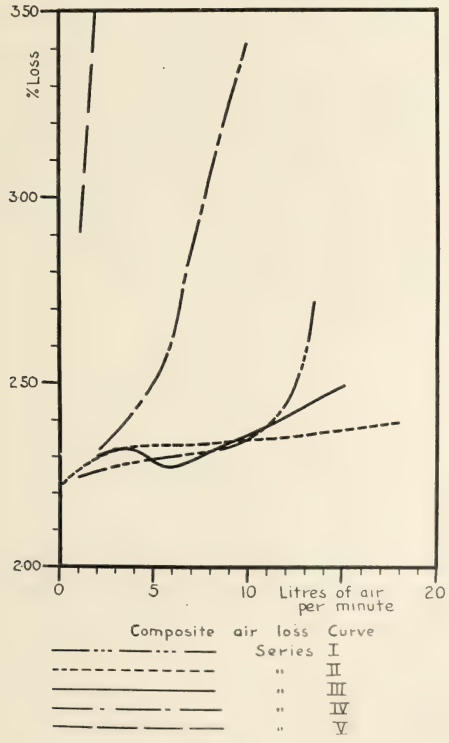
TABLE NO. 5. SERIES 5. TEMPERATURE 910° C. JET OF AIR DIRECTLY APPLIED TO CUPEL AT 1 INCH.

Exp. No.	Time min.	Air litres per min.	Loss %	Remarks
1	3½	15.0	7.57	Some feathers, lead spit
2	5	9.8	6.75	Lead bubbling, no spitting
3	5½	6.7	6.30	" " " "
4	6½	4.3	5.13	
5	11	2.0	3.46	
6	12	1.3	3.39	
7	16¾	0.5	2.70	

very high draft, which rapidly carried away volatilized litharge as it formed. That such conditions as here depicted never occur in practice is true, no doubt; this experiment has been pushed to an extreme to show the bad effect of a heavy supply of air to a cupellation.

Conclusions—Volume of Air.

For purposes of comparison the five loss Curves 2—6 have been plotted to one scale in Curve 7. In these there is only one exception



Curve 7.

to the conclusion that the more air is passed through the muffle, for each set-up, the higher will be the loss. This is in Series 3, and there only for a small part of the curve. The fact that the higher air supplies cooled down the cupel slightly, and hence tended to lower the loss, has been neglected. This means that the upward trend of each curve has been held to a minimum, and if the temperature could be corrected for this cooling effect the curves would rise more steeply. The conclusion drawn, then, may be considered to be safely on the conservative side. Therefore, under these conditions the less air supplied to a cupellation, above the amount just necessary to carry it along at the prevailing temperature of the muffle, the lower will be the loss.

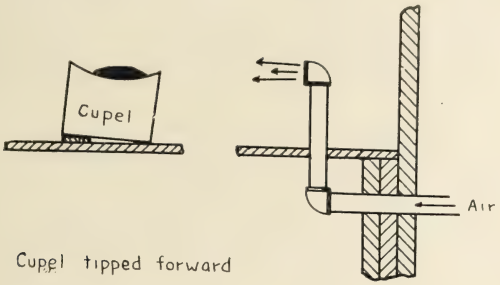
Conclusions—Method of Application of Air.

The argument may be justly raised, that it is the amount of air coming in actual contact with the lead which should be considered or measured, rather than that pouring through the muffle. If we had any means of determining that quantity, we would probably find that the different means used for projecting air across the cupel would cause no difference in loss, for the same amount of air touching the molten bath, although the air in Series 5 would have to be low indeed to compare with Series 1-2-3. Since this measurement did not appear to be practicable, we must be content with the methods used, knowing that they at least offer a basis for comparison understandable to those performing commercial wrok. The conclusion from this work, then, is that when air is in its most diffused state, having a low uniform velocity throughout the cupellation, low losses and close agreement between assays otherwise run under comparable conditions will be obtained. The converse is that high and varying velocities of air currents cause high and varying losses.

SERIES 6—TIPPED CUPELS.

This short series was tried to see if a slight tipping of a cupel in any direction would create differences in losses. It had been observed in work in gas, coal and oil fired furnaces that the muffle floor was usually uneven, due to warping, encrustations of slag, lumpy sand, or bone ash. To place a row of cupels on such a surface, and have their tops horizontal and at the same level was nigh impossible unless a deep bed of bone ash was used. Even then the operation was uncertain. That differences in loss due to variations of cupel level would be greatest in a strong draft was obvious, so Series 4 system of air supply was used, in order that positive conclusions might be made. The cupels were tipped in the manner shown in Fig. 12.

Those "tipped forward" were tilted towards the supply pipe by raising the far side ⅛ of an inch; those "tipped backward", exactly in the opposite direction. The tilting was accomplished by a tapered iron washer. Positions in the muffle were standardized by cementing the washer in place and setting the cupels in the usual slot provided for their constant location. Before the results were determined, a firm



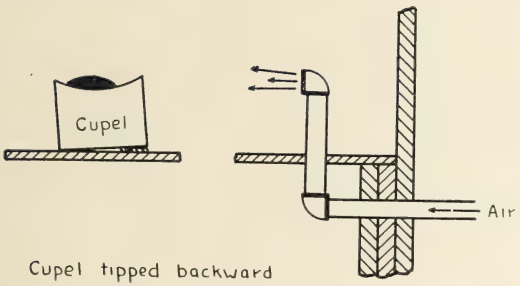


Fig. 12.

TABLE No. 6. SERIES 6. TEMPERATURE 910° C. CUPELS TIPPED.

Cupels Tipped.	Exp. No.	Air litres per min.	Loss %	Average Loss %	Remarks.
Forward	1	3.3	2.42		Very slight feathers
„	2	3.3	2.46		Slight feathers
„	3	3.6	2.41		„ „
„	4	3.6	2.38		„ „
			9.67	2.42	
Back	5	3.7	2.68		No feathers
„	6	3.6	2.53		„ „
			5.21	2.60	

conviction existed that those "tipped forward" would give the higher loss. A glance at the results in Table 6 shows that this was erroneous.

The losses given in Series 4 for the air supplies here used, range from 2.36 to 2.39%. Since all the losses here are higher, it appears that tipping a cupel either forward or backward is a mistake. Strangely enough, tipping backward away from the direct air blast gave the higher losses. The anomaly is left unexplained; it is only one of many apparent contradictions that arise. The cupellations with feathers, those with forward tipped cupels, gave the lower losses here, however.

SERIES 7—DUMMY CUPELS.

The practice of placing a row of uneven cupels, commonly called "dummies", in front of a charged row is so common that it was thought worthy of investigation. What effect has such an arrangement upon loss using strong drafts? The disadvantage of eddies of air near a cupellation has been established. Do not dummy cupels tend to create such eddies?

A series, using different heights of protecting cupels between the charged one and the air supply pipe, was performed, utilizing the Series 4 set-up. The results appear in Table 7. All the tests were made with

TABLE No. 7. SERIES 7. TEMPERATURE 910° C. VARIOUS HEIGHTS OF DUMMIES.

Exp. No.	Height of dummy-inches.	Loss %	Average Loss %	Remarks.
1	½	2.51		Feathers
2	½	2.54		"
3	½	2.57		"
		7.62	2.54	
4	¾	2.57		"
5	¾	2.85		"
		5.42	2.71	
6	1	2.38		
7	1	2.34		
		4.72	2.36	
8	1¼	2.34		
9	1¼	2.40		
		4.74	2.37	
10	1½	2.35		
11	1½	2.41		
12	1½	2.38		
		7.14	2.38	

3.4 litres of air per minute. The times of cupellation are omitted due to the difficulty of spotting the completion of cupellation through the observation tube, using dummies higher than the 1", or standard.

This work shows that:—

(1) No test with any height of dummy gave a loss lower than with an unprotected cupel.

(2) A dummy cupel, lower than the charged one behind it, greatly increased the loss. This was probably due to an increased supply of air to the lead, the air being deflected upwards, thus causing local eddies.

(3) A row of cupels placed in front is a bad procedure in practice if they are low, irregular in height, or irregularly spaced.

The primary purpose of dummies is to protect the front row of cupels from undue chilling action from the air supply, and consequent danger of freezing. A better method than using dummies is to place a rectangular clay bar, of uniform height and smooth surface, in front. It should be slightly higher than the cupels. With this, the air passing over it, is given a uniform deflection. It does not cause the current to break into eddies, thus favoring or otherwise affecting one cupellation differently from another. The continuous protection across the row gives more uniform conditions than dummies give.

SERIES 8—RINGS ABOUT CUPELS.

Deep cupels have been recommended by a number of authorities, to giving a low loss, as Rose (m), and Bugbee (n). They should give lower losses than shallow ones if a high draft is used, because their high edge or lip would prevent the air from striking the lead directly, thus

TABLE NO. 8. SERIES 8. TEMPERATURE 910° C. RINGS ON CUPELS.

Exp. No.	Height of ring—inches.	Air litres per min.	Loss %	Series 4 Loss %	Remarks.
1	9/16	3.8	2.06	2.39	Time about 28 min.
2	9/16	3.8	2.05		
3	9/16	8.0	2.25	2.94	
4	6/16	4.3	2.13	2.42	
5	6/16	6.7	2.24	2.71	„ „ 23¼ min.
6	3/16	4.7	2.22	2.45	
7	3/16	8.3	2.58	3.01	

diminishing the air supply, prolonging the cupellation time, and lowering the loss. It was not easy to make standard cupels (*i.e.*, with the same shape of cup), and vary the rim or edge height. It was feasible, though,

to place a ring on top of the regular cupels, thus closely imitating deep cups. One advantage in doing this lay in the ease with which the same ring could be ground down to various heights, and the same one be used for all the trials.

In Fig. 13 is represented a ring on the top edge of a cupel. The joint between it and the cupel was not air tight, but it was close fitting. The ring was made from the top of an alundum extraction thimble. It was at first used with a height of 9/16", then at 6/16", and lastly at

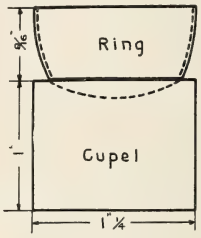


Fig. 13

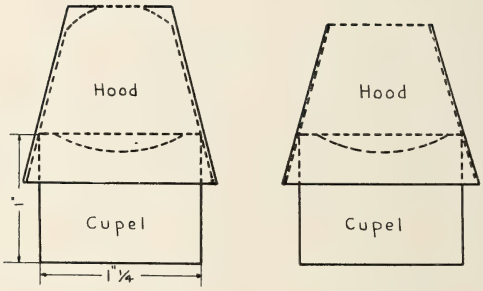


Fig. 14(a) Fig. 14(b)

Fig. 13—14 (a-b)

3/16". The Series 4 set-up was again utilized. The figures for this Series are in Table 8. Times of cupellation could not be taken properly here. As a means of comparison the Series 4 losses are inserted.

This work shows that:—

(1) The higher the ring, the lower was the loss.

(2) The use of rings, at all heights and air supplies, produced lower losses than without.

(3) Deep cups lower the loss.

(m) Rose, T. K.—"Assaying Gold Bullion", E. & M. J., 80; 1905.

(n) Bugbee, Ed. E.—"Text Book of Fire Assaying", 1922.

SERIES 9—HOODS OR VERY HIGH RINGS OVER CUPELS.

The ring experiments just related gave such positive results that it was considered advisable to proceed a step further in this particular branch of the research and protect the lead from the air, up to the very limit, to make the cupellation very slow, in order to ascertain how low a loss could be obtained at this temperature of the muffle blank of 910°. This was done by placing a hot annealing cup with various holes in its base, upside down over the cupel, after it had opened in the B Muffle. Series 4 supply pipe was used. The cup was placed on the cupel while hot, because cold ones froze the buttons. The buttons would not open with the cup in position.

These cups or hoods sat over the cupel as pictured in Fig. 14 (a). The junction of cupel and hood was fairly tight, much better than with the previous rings, and we may conclude that practically no air reached the button through it.

Test 1.

Four small holes, each about 1/16" in diameter, were drilled through the base of the cup. The button was opened and the hood placed over the cupel. The button froze. Here the litharge fumes filled the cup; the oxygen therein was used up, and oxidation ceased.

Test 2.

The holes were enlarged to 3/8" in diameter and the test was repeated. Air was supplied at 3.9 litres per minute. The cupellation proceeded to the end and lasted 42 minutes, giving a loss of 1.55%. It was necessary to do several of these, removing the cover at a later stage each time, to determine the time required. The loss of 1.55% is a very low loss indeed, for a cupellation run at 910° C. cupel temperature (blank), this low loss might be anticipated from the length of the cupellation. Almost invariably, in all of the work, the longer the time of cupellation the lower was the loss.

Test 3.

The base of the cup was cut off as is shown in Fig. 14 (b). The wall of the hood extended 8/16" above the cupel, a deep cup, to be sure. Air was admitted to the muffle at 8.9 litres per minute and from the pipe directed at the cupel. The cupelling time was 33 minutes, the loss 1.78%. In Series 4, without a hood, at this rate of air the loss was 3%, and feathers were present there. Here no feathers formed, and the loss was 1.22% less. The work on hoods shows that they diminish the loss but increase the time.

SERIES 10—THE EFFECT OF OXYGEN.

To illustrate the effect of oxygen as compared with air with its four-fifths of inert nitrogen, a few experiments were carried on in the twin muffles using oxygen gas. The oxygen was admitted just as air had been, and under the three set-up conditions of Series 1, 4 and 5. All other conditions, such as muffle, temperature, etc., were the same as described under the former series. Oxygen was supplied from a cylinder through the Precision Meter and allowed to flow through the muffle for several minutes before the beginning of a cupellation to sweep out the air present. The results of these tests appear in Tables 9, 10 and 11.

TABLE No. 9. SERIES 10. TEMPERATURE 910° C. SERIES 1 SET UP WITH OXYGEN.

Exp. No.	Time minutes.	Oxygen, litres per min.	Equivalent air, litres per min.	Loss %	Comparative loss with air %	Remarks.
1	7	1.2	5.7	7.07	2.29	No spitting of lead.
2	11½	0.54	2.6	4.15	2.26	
3	17	0.25	1.2	2.91	2.24	„

TABLE No. 10. SERIES 10. TEMPERATURE 910° C. SERIES 4 SET UP WITH OXYGEN.

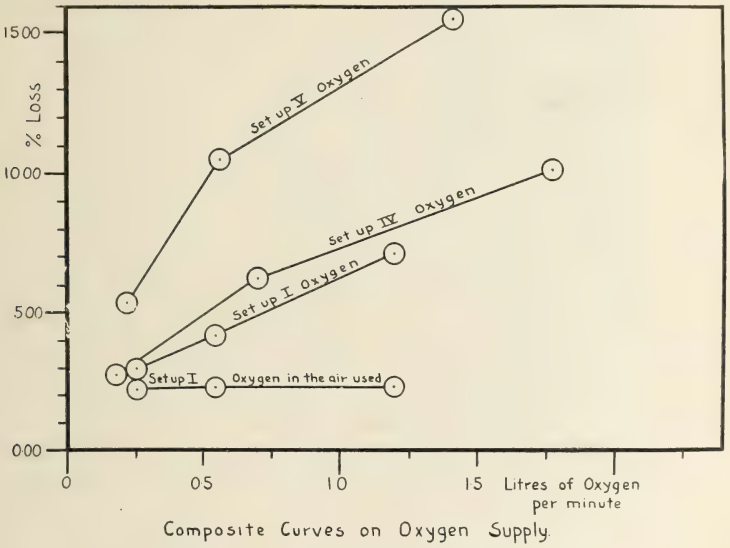
Exp. No.	Time minutes.	Oxygen, litres per min.	Equivalent air, litres per min.	Loss %	Comparative loss with air %	Remarks.
1	15¾	0.18	0.86	2.85	2.30	Lead quiescent.
2	7	0.70	3.3	6.23	2.36	Lead bubbling.
3	5¾	1.78	8.5	10.11	3.05	Surface lead temp. 1240° C.

TABLE No. 11. SERIES 10. TEMPERATURE 910° C. SERIES 5 SET UP WITH OXYGEN.

Exp. No.	Time minutes.	Oxygen, litres per min.	Equivalent air, litres per min.	Loss %	Comparative loss with air %	Remarks.
1	2.1/6	1.41	6.7	15.48	6.10	Lead spit badly, PbO unabsorbed.
2	4	0.56	2.7	10.51	4.18	Some spitting, Ag beadlets left.
3	9	0.22	1.0	5.35	3.05	No mechanical losses.

The lead bath, under the influence of oxygen at the higher supplies used, grew almost incandescent and surface temperatures of 1200° C. and over were obtained. Even in an atmosphere of almost still oxygen

the loss was 2.91%, or 0.67% higher than in the standard where the loss was 2.24% using air. Under a draft of oxygen the losses were, of course, very high. These were due in some measure to spitting, and to small beadlets left behind on the cupel surface. Beads finished with amazing rapidity; the cupels were highly colored with the heavy green stain which accompanies a high silver loss. The cupellation No. 1 of Table 11, using Series 5 set-up and having 15.48% loss, formed litharge more quickly than the cupel would absorb it. This pooling of litharge about a bead, it will later be shown, gives losses almost as high as this when only air is used. Some of the beads were molten for half a minute after removal from the furnace, thus showing the intense heat of oxidation that had existed.



Composite Curves on Oxygen Supply

Curve 8.

In the Tables, the losses occurring with amounts of air having an equivalent oxygen content to that here used are inserted to show the protection the inert nitrogen gives. The losses are graphed in Curve 8, to which is added Series 1 losses using air supply for comparison. Oxygen increases the rate of oxidation, and the losses, it decreases the time of cupellation.

In three experiments where oxygen was supplied directly to the cupel, from a vertical tube just through the muffle roof above the cupel, the losses at 1, 1.9 and 2.1 litres of oxygen per minute were respectively 13.8, 37.3 and 37.2%. The cupellation times were 4 minutes for the

first and 2 minutes for the latter. The two highest loss cupellations had a fine matting of feathers. The beads were imbedded in the cupel, and litharge pools were present. The thermocouple above the blank cupel to one side of the cupellation showed 951° C.; the blank cupel then was at 906° C. For these high losses, beadlets, sprouting and the litharge pools were in part responsible.

Some tests were run using nitrogen gas to dilute air, and in general these gave very unsatisfactory non-checking results. Apparently low losses were obtained, but this was likely due to lead left in the beads. The addition of a few per cent. of nitrogen to air greatly decreases the rate of oxidation. Passing nitrogen through the muffle at 1 litre per minute, with the only oxygen available being that present in the small amount of air which leaked into the muffle, the cupellation time was 1 hour and 8 minutes and the loss 1.26%. The average muffle blank temperature here was 907° C. The button was no brighter than the cupel. This was because of the very low oxidation. About 2 minutes before the end, the nitrogen supply was stopped, as the cupellation appeared too cool to finish properly. The door was opened and air admitted. The bead brightened faintly, gave a short play of colors and a weak blick. With 1 litre of air and no nitrogen, the loss was 2.28% with a blank cupel temperature of 906° C. With two litres of air and 4 litres of nitrogen per minute, the cupelling time was 35 minutes and the loss 1.36%, with a blank cupel temperature of 903° C. The play of colors lasted for 12 seconds, followed by a good blick. In these runs the beads were attached. In other runs under similar conditions to the above, the losses were much lower, but the beads were not attached, being loose in the cupel, an evidence of containing lead. To one accustomed to the usual behavior of a cupellation with air, the addition of nitrogen with the consequent slowing up of oxidation gives a condition somewhat analogous to cupelling with a basic cupel like a Morganite as compared with bone ash; the cupellations run cooler at the same muffle temperature.

MUFFLE DRAFT.

While it is generally recognized that chimney draft, as affected by weather, wind and other atmospheric conditions, is an important factor in furnace work, the influence of changes in muffle draft produced by slight alterations in the adjustment of doors, dampers, burners and other accessories, and by the conditions of the linings and supports, is frequently overlooked, or not given the attention which it deserves.

DRAFT TEST ON A GAS MUFFLE.

To illustrate these variations some draft tests on a No. 8 Fletcher Russell Gas Muffle are given. This particular furnace was selected because it had just been overhauled and supplied with a new muffle. It is shown in Fig. 15. It was heated by eleven bunsen type burners. Each had its gas tap, and the air for combustion was adjusted by a sliding sleeve. These burners are referred to by numbers 1—11. Gas

Fig. 15.

to these was supplied from a 1¼ inch city gas pipe. The flames passed upwards around the sides and back of the muffle, and out through two five inch diameter pipes at the top, each supplied there with a slide or damper. These pipes joined to a six inch diameter pipe at two feet above the furnace, which in turn joined to a main pipe 8 inches in diameter above, and leading to a main chimney flue some five feet away. The muffle 13 × 8.5 × 5.5 inches had two holes in the rear 1½" in diameter, and leading to the back flame passage. The

usual clay doors were removed, and over the opening was held an asbestos plate, to which was attached horizontally a copper tube 2¾ inches in diameter and 4 feet long. Midway of the tube was located a Feuss anemometer. This just filled the tube. The anemometer dial protruded through the side of the tube and could be read during the tests. The atmospheric conditions as given in Table 12 were obtained from the Meteorological Office at Toronto.

The draft readings were of from one to two minutes' duration, to minimize slight variations due to changing chimney draft. All doors, as well as fume cupboards, of the room were closed, and no other furnaces were in operation at the time. The anemometer fan did not move freely with quantities of air below about 30 litres per minute, hence any readings in Table 13 marked O show a rate between ± 30 litres.

TABLE No. 12. STATEMENT OF TEMPERATURE, WIND AND RAIN.

Month 1924	Day	Hour P.M.	Temp. °F.	Wind Dir.	Wind Vel. m.p.h.	Rain.
April	3	1	47	S.W.	16	None
		2	48	S.	12	
		3	49	S.W.	16	
		4	49	S.	12	
		5	49	S.W.	12	
		6	47	S.W.	14	

A perusal of the information in Table 13 shows how draft through a muffle varies, when making the kind of adjustments one usually does, during a cupellation, to obtain conditions desired. Here the door was not altered as one would during a cupellation; it was closed throughout. This eliminated a very important factor, causing variation in draft in ordinary work. It seems plain, then, that unless each furnace is adjusted the same for each cupellation and with the same natural chimney draft, or by another set of combinations that will give the same resultant effect, the muffle draft must change greatly from time to time. In view of the serious effects of varying air supply, already shown, how then can consistent work be done?

As far back as 1867, Percy (o) described furnaces equipped with a separate pipe from the muffle to the flue, and equipped with a wing damper. Such a furnace was used by Arnold T. Watson at the Sheffield Assay Office. Rose (p), in 1905, found that assay pieces near the side of the muffle suffered appreciably greater losses than those in the middle line, especially at the front and back. In consequence, the

(o) Percy—"Metallurgy of Lead," 1880.
(p) Rose, T. K. E. & M. J.—Vol. 80, Sept. 16th, 1905.

draft of air through the muffle was made independent of the draft through the fuel chamber of the furnaces at the Royal Mint. He pointed out that this was an important feature, which should be adopted in all muffles. Smith (q) also describes the Royal Mint gas muffles, and states:—"The muffle is provided with a slit or a number of small holes about 3/8 inch in diameter, at the back, in order that by means of the furnace draft a current of air may be constantly passing through the muffle. It is necessary that the position, number and size of the holes in the muffle should be carefully adjusted according to the draught of

TABLE No. 13. MUFFLE DRAFT—GAS FURNACE.

No.	Furnace Conditions.	Air litres per min.
1	Before lighting gas taps—window closed, dampers open.	57
	5 minutes later.	58.5
	5 „ „	55.5
2	Window open 1 foot at top	82.5
3	Window open 2 feet at top (and to No. 14)	76.7
4	Taps 1-3-5-7-9-11 lighted—Main gas tap on half way.	104.4
	5 minutes later.	90.9
	5 „ „	88.5
5	Main gas tap on full.	63.3
	5 minutes later.	59.4
	5 „ „	57
	5 „ „	58.2
	5 „ „	59.4
6	Taps 7-9-11 on.	82.5
7	All Taps off.	75
8	Taps 1-11 on.	57
9	Taps 1 to 10 lighted, 11 off.	42.5
10	Taps 2-4-5-6-7-8-10 lighted, 1-33-9-11 off.	57
11	Taps 1 to 6 lighted, 7 to 11 off—Temperature 800° C.	77.4
12	As 11—but front damper in, back damper out.	58.4
13	As 11—but front damper out, back damper in.	0
14	Taps 1-3-5-7-9 lighted, others off, dampers as in 13.	75
15	As 14—but window closed.	68.4
	5 minutes later.	72
	5 „ „	72.6
	5 „ „	73.8
16	As 14—window open 2 feet.	81.9
17	Taps off, window closed.	72.6
	10 minutes later.	75
	10 „ „ Temperature 650° C.	72
	10 „ „ now affected visibly by wind changes.	77.4
18	1 hour later—6 p.m.	64.5
19	Next morning—10 a.m.	52.5

(q) Smith, E. A.—"The Sampling & Assay of the Precious Metals," 1913.

the muffle and other circumstances." Furnaces with similar pipes connecting the muffle to the chimney are shown in Manufacturers' Catalogs to-day, where it is claimed that these will give fast cupellations. They undoubtedly will, but they may also give high and variable losses, unless with high chimney draft they are throttled down. Such pipes are a distinct advance, but, better still, they should be connected to an independent steady suction from a fan. Then for particular settings of a wing damper, or by control of the fan speed, draft suitable for the work at hand could be obtained at will, and be repeated from day to day, thus giving a steady air supply and promoting consistency in the losses.

COAL MUFFLE FURNACE DRAFT TESTS.

To further illustrate how various settings of a furnace affect muffle draft, anemometer tests were made as before for quantity of air passing through the lower muffle of a two muffle U.U. coal furnace as shown in Fig. 16. The upper muffle door was left in place, closed. Over the

Fig. 16.

opening for the lower door, with its clay door removed, was placed the asbestos plate, to which was held the anemometer tube. The fit of the plate to the furnace front was not good, so that some air leaked in about the edges. The contact was kept unchanged throughout the tests, so that while more air passed through the muffle than the anemometer indicated, the poor contact against the bricks did not introduce a serious variable. The furnace had the usual fire and ash doors at the rear. In the smoke flue above the muffles leading to the chimney proper was a clay draw-bar of 2 × 8 inches in cross section for controlling the flue draft. Above the muffles in front, there was an opening leading to the chimney pipe, to carry away any fumes or smoke escaping through the muffle fronts. The exit holes at the rear of the muffles were two in number, each about 1½ inches in diameter. This furnace had not been fired for months before this test. The atmospheric conditions for Toronto were obtained from the Meteorological Office. These are in Table 14.

TABLE NO. 14. STATEMENT OF TEMPERATURE, WIND AND RAIN.

Month 1924	Day	Hour	Temp. °F.	Wind Dir.	Wind Vel. m.p.h.	Rain inches.
June	23	1	76	S.	12	
		2	71	S.W.	12	0.25 (1.30 to
		3	77	S.W.	3	2.0 p.m.)
		4	77	W.	16	
		5	78	N.W.	19	
		6	78	W.	16	

The fire was started at 12 o'clock noon, and by 3 o'clock the muffle was at 900° C., when the tests were begun. Before lighting the fire, a candle was placed close to the crack between the regular lower muffle door and the furnace wall. A nearby window was open, and the effect of the light wind on the leaves of trees was visible. With still leaves, the candle flame was practically vertical, but as the leaves moved, the flame bent inwards, showing the increase of draft with a freshening wind. On other occasions, the change of velocity and direction of litharge fumes from cupellations has been noted to vary as wind outside the building changed in intensity, as evidenced by the sound thereof, showing again that chimney draft is a variable affecting muffle draft. It seems, however, to affect the muffle draft more when cold, than when a volume of smoke, flame or gases fill the pipes.

The air volume tests are given in Table 15. This shows the effect of some combinations of ash and coal doors, slide bar positions firing with fuel, and window location. Each adjustment has an important

effect on the amount of air drawn through the muffle. The condition of the fuel bed, whether fuel has just been added or not, greatly affects muffle draft. The smoke entering a muffle when fresh fuel is added gives a reducing atmosphere. It is a quite common practice to open the coal door to cool down a muffle during cupellation; this certainly eliminates the muffle draft also; compare in the Tables Nos. 5-6, 10-14, 13-14. Tests 16-24 show very plainly the importance of giving attention to the slide bar or check, above the muffles in the smoke flue. If we kept our furnace adjustments, doors, dampers constant throughout a run, the muffle draft still varies due to changes in fuel bed and flue draft. The direction and apparent velocity of the litharge fumes from the cupellation is at best only a rough guide as to the amount of air passing

TABLE No. 15. MUFFLE DRAFT. COAL FURNACE U.U.

No.	Furnace Conditions.	Air litres per min.
1	No fire. Back doors closed. Average for 5 minutes. Maximum variations per minute was 18 litres.	53
2	Fire started at 12 a.m. noon.	
3	Coal door closed. Ash door open, slide bar out 2". 2 p.m. Coal added, window open 1 foot.	0
4	Coal door closed. Ash door open, window and slide bar left unchanged to No. 14. 3 p.m., 900° C.	267.3
5	Coal door open. Ash door closed.	48 back draft.
6	Coal door closed. Ash door closed.	271.5
7	Coal door open. Ash door open.	79.5
8	Coal door open. Ash door open. Coal added.	69.3 back draft.
9	Coal door closed. Ash door open.	94
10	Coal door open. Ash door closed.	50.3
11	Coal door closed. Ash door closed.	292
12	Coal door closed. Ash door open.	90.7
13	Coal door open. Ash door closed.	0
14	Coal door closed. Ash door closed.	280.5
15	Coal door closed. Ash door closed. Window closed.	259.5
16	Doors closed—Slide bar out 1 inch, approx.	196.7
17	Doors closed—Slide bar closed.	0
18	Doors closed—Slide bar out ½ inch, approx.	156.
19	Doors closed—Slide bar out 1 inch, approx.	192.
20	Doors closed—Slide bar out 2 inch, approx.	277.5
21	Doors closed—Slide bar out 3 inch, approx.	333.8
22	Doors closed. Window open.	349.5
23	As 22, but slide bar removed entirely.	296.6
24	As 23, anemometer over slide bar opening to measure air drawn in there.	401.2
25	Q.Q. muffle furnace in next room, on another chimney, no fire, doors closed, slide bar open 2 inches, Air to muffle.	57.

through the muffle. For a furnace with a high draft we can use small exit holes at the rear, but these encourage high velocity currents to them, over some of the cupellations and eddies in the muffle. The only simple way to have a uniform muffle draft is to draw the air through a row of holes, or a horizontal slit across the rear width of the muffle, independently of the fire or fuel, by a pipe leading to a fan, or similar suction.

CUPELLATION IN A GAS MUFFLE.

As examples of the application of the information which has been set forth in the foregoing pages, several runs were made in a No. 8 Fletcher Russell gas fired muffle furnace. Its muffle did not have separate air pipes for air control, just a 1½" round hole, at the muffle rear and entering the combustion passage to the chimney. Air measurements were made immediately before and after the runs by the method as explained in the muffle draft work; the averages are given. Temperatures of the air above the cupellation were taken every minute with a Cambridge Platinum Resistance Pyrometer. The couple tube was supported by the lower half of the clay muffle door, in a groove corresponding to its cross section. The couple end of the tube was about 1" above the central cupel of a row of five, and fixed in location throughout the tests. This has been such a favorite location in much experimental work which has been published, that it was used here, but like many such, merely serves in a relative way to compare one cupellation with another as to temperature,—where the same set-up is used in each case. The cupels were placed in the same position in each run, and rested on a fire clay slab a half an inch in thickness; thus the surfaces were uniform in height, and level.

The results of the various tests are in Table 16. The buttons were placed quickly, and in each case opened at about 885° C. In runs 1—4 the full draft of the muffle for the day was utilized, with the two check dampers of the chimney pipes withdrawn. This was not a high draft as muffle drafts go, as on other occasions drafts of as high as 12.5 cubic feet per minute were measured. In runs 6—9 the air supply was reduced to an amount that would operate the anemometer continuously, yet not be in danger of stopping due to the slight variations in flue draft on this day. This was accomplished by adjusting the check dampers well in, and placing an asbestos plate loosely against the exit hole of the muffle. The protecting bar used in the latter runs was placed in front of the row of cupels; it was a smooth fire clay door 1¼" high, 3" wide and just reaching each muffle wall. Its top was about ¼" above the bone ash cupels used. Just as soon as the buttons

Table No. 16. Cupellations in a No. 8 Gas Furnace.

No.	Average Temp. °C.	Finishing Temp. °C.	Air per min. cu. feet.	Time of Cupellation mins.		% Silver Loss. 1	2	3	4	5
1	777	758	5.2	17	No bar used. Door placed so that most air went to the left where most feathers occurred.	2.06	2.01	1.85	1.89	1.87
2	777	785	5.2	17½	No bar used. Door was uniform, not favoring one side. A few feathers on all.	2.05	2.25	1.90	2.05	2.08
3	787	785	5.2	13-16	Irregular dummy cupel protection and door placed so that most air went to the right. No. 1 had some feathers.	2.19	2.58	2.37	2.72	2.54
4	790	792	5.2	19	Bar used in front of cupels. Less feathers than in 2.	2.04	1.99	1.81	2.07	2.06
5	850	834	1.8	21½	Bar used. No feathers.	2.01	1.99	1.91	1.96	1.96
6	838	809	1.3	22½	Bar used. A few feathers.	1.53	1.45	1.50	1.43	1.47
7	813	798	1.0	29½	Bar used. Heavy feathers.	1.29	1.40	1.19	1.35	1.23
8	815	823	1.0	30	Bar used. Heavy feathers.	1.36	1.39	1.26	1.36	1.35
9	825	827	1.0	28	Bar used. Delayed opening. Feathers scant.	1.69	1.77	1.73	1.72	1.75

opened, the gas flames were shut off for a couple of minutes to lower the muffle temperature; they were then relit, and adjusted for a low flame. At this stage the upper half of the door was placed on the lower half, and out about one fourth of an inch. As the cupellation proceeded, the heat supply was adjusted so that the temperatures of the various runs would be comparable. This was accomplished by adjusting the main gas valve; the individual burners from front to rear were not altered during the runs.

The tests at the lower air supply gave lower losses than those at the higher rate, notwithstanding the fact that the former had the higher average and finishing temperatures of the air passing through the muffle, as indicated by the pyrometer. Runs 1—2 and 4 at the higher rates were performed at lower average and finishing temperatures than runs 6-7-8, at the lower rates. The clay bar acting as a store house of heat, probably influenced the temperatures taken, and differently at each air supply. With the lower air supplies, the temperature could be maintained with a lower gas flame, but of course the cupellations took longer. At the beginning of all the runs the temperature was lowered as far as seemed safe without being in danger of freezing. In none of the assays was freezing imminent at any time. This was safeguarded. All beads blicked, and were attached to the cupel.

The higher the draft through a muffle the more heat is carried away, *i.e.*, the muffle is chilled, also the cupels. When the cupel is not hot enough to absorb the litharge flowing onto it, pooling of litharge the forerunner of freezing, begins. At the same time a high air supply increases the rate of oxidation. This increased local heat supply does in part counteract the cooling down of the cupel. The cooling effect of air may be insufficient at high rates to more than balance the heat imput from the furnace and from the oxidation heat. There may be active oxidation of the alloy with high losses occurring, and at the same time litharge gathering about its base on a cool cupel. Under these conditions feathers may be forming on the cupel. Once freezing is apparent, the assayer urges the fire to increase the muffle and cupel temperature. The door will be closed. This slows down the oxidation rate, under a diminished air supply less heat is liberated per unit of time at the cupel. Once freezing sets in, it will likely go to completion before the cupel can be heated sufficiently to absorb the pool of litharge formed. Had the air supply been reduced earlier, freezing would not likely have occurred at the temperature then prevailing. Operating with open door, the cooling effect of a high draft playing directly on the cupels may more than counteract the heat from the high rate of oxidation; this is the forerunner of freezing. This condition was not present here.

In all the runs save Nos. 3, 6 and 9, the central cupel gave the lowest loss in the row. This was likely because of the protection of the pyrometer tube above it, diminishing the air supply by diverting it to the sides. In each case the central cupel took longest to cupel.

In run No. 3 old cupels of different sizes, some broken, were placed in front of the row of cupellations, in a manner to deflect air to each differently. This gave the irregularity and the high losses shown.

Run 9 was planned to ascertain the effect on loss of a delayed opening of a button or beginning a cupellation at too low a temperature to open it. A hole was put through the side of the furnace, and into the muffle. A clay tube was luted to this hole. A cupel was placed on the muffle floor about two inches behind the regular row so that it could be viewed through a glass placed over the external opening of the tube. With the air temperature at 782° C. the regular row of cupels was charged, also a blank lead button was placed in the rear cupel. The doors were tightly closed, and the temperature raised slowly until in 15 minutes it was 834° C. The top door was opened for 6 minutes; the temperature was then 831° C.; none of the buttons had opened. The door was again closed. At 25 minutes from the start the dummy uncovered, the door was opened at the top; only the left cupel had opened. The central temperature was 871° C. The other buttons were all opened at 27 minutes. The actual cupellation then proceeded with the upper door out ¼ of an inch, as in the other runs. The temperature was lowered; at 35 minutes it was down to 801° C. Then the temperature was increased until at the blick it was at 827° C. The actual cupelling time averaged 28 minutes; during this period the average temperature was 825° C. The temperatures here during the cupellation were comparable with those of run No. 8, but it should be observed that the opening temperature of run 9 was about 10° below No. 8. The No. 9 losses average 0.39% higher than those of No. 8.

Ordinarily if some buttons on charging do not open readily, the temperature is raised until they open. These buttons give higher losses than their mates, and the cause is usually thought to be due wholly to high temperature. The increase in loss may also be attributed in part to a long contact of a thick pasty litharge coating over a molten interior of lead silver. This condition was further investigated in experiments to be described in Part III.

CUPELLATIONS IN A COAL MUFFLE.

It is much more difficult to make comparative tests in a coal than in a gas fired furnace. The conditions of the coal bed vary so greatly from time to time, we cannot say that any two runs are just alike.

The results of two tests in the U.U. muffle with a high and a low air supply are given in Table 17, to show comparisons similar to those with the gas furnace. Temperatures as before were taken with the pyrometer couple about 1 inch over the cupels, but it was moved from cupel to cupel during the test so that the tendency for its position to cause local variations in loss or time to any one cupel was eliminated. The readings were taken each minute, and the average temperatures over the test are given.

In No. 1 run the draft was high, 7.4 cubic feet per minute before the test, with both rear doors closed. The cupellations, a row of nine with dummies at each end, were placed about one fourth way back in the muffle. These were protected in front by a smooth clay bar placed a half inch in front of the cupels, and with its top about a fourth of an inch above them. The muffle floor was somewhat uneven, so that the relative heights of the cupels, and their general level varied slightly. The opening temperature was not taken, but was sufficient to open all the cupels in less than a minute. The fumes hurriedly passed almost in a straight line to the exit hole. At this stage the coal door was opened, to cool the muffle and reduce the draft; the fumes still passed out readily, however. Eight empty crucibles at the muffle rear were removed and replaced by cold ones. Cold iron moulds were worked back over the cupels, to give a cool drive; up to this stage the pyrometer tube rested on an end dummy cupel. During the run, and until about a minute before the blick, the regular clay door was laid flat in the muffle entrance. The pyrometer tube was passed back and forth over this, to take readings about 1 inch above the cupels. At the end the crucibles were removed close to the cupels, a practice used to ensure a temperature rise at the finish. During the last half minute of the cupellation the door was placed upright.

In the second run under a very low draft, the conditions of operation were the same, except that as soon as the buttons opened, the two exit holes at the rear of the muffle were each loosely plugged with a small crucible, thus greatly reducing the draft. During the run the fumes rose well towards the muffle crown, and passed slowly to the rear. At times, however, they moved to the front, and escaped upwards through the smoke hole above the muffle. This then was a very low draft condition, but with the large muffle and open door, there was a ready air supply to the cupels.

Here again the lower air supply cupellations run at higher air temperatures gave the lowest losses. The slight increase in loss from left to right is a noteworthy point here, for both low and high air conditions. It was probable, that in "stoking", one corner of the fuel bed

TABLE No. 17. CUPELLATIONS IN AN U.U. COAL FURNACE.

No.	Average temp. °C.	Air.	Time of cupellation min.	Feather Conditions.	% Silver Loss. 1	2	3	4	5	6	7	Av.
1	785	High	15½	Feathers scant irregular, small and close.	1.93	1.89	1.99	1.99	2.04	1.97	2.07	1.98
2	820	Low	19½	Feathers flaky, regular and heavier than in 1.	1.58	1.60	1.53	1.59	1.58	1.62	1.68	1.60
				Difference	0.35	0.29	0.46	0.40	0.46	0.35	0.39	0.38

was constantly favored with fuel, thus giving a higher temperature at one side than at the other. Or, the difference in loss may have been due to the muffle having shifted slightly to one side, thus allowing more combustion to take place at the right than the left. Slight, unnoticed causes like this often produce greater effects than it is usually expected they would. Although the average air temperature is 35° C. higher in the low air supply run, the average loss is 0.38% lower.

SOME PRACTICAL CONSIDERATIONS.

Much experimental work was done using different kinds of doors, with many types of air openings, in an attempt to give all the cupels in a muffle the same air supply when several rows of cupellations were run. Various types of deflector and baffles within the muffle were used in an attempt to obtain uniform losses from front to rear, without varying the muffle temperature as between front and rear. Only partial success was given by the heat of these artifices.

In practice many rows of cupellations are performed at once. In a furnace giving a higher temperature at the rear than at the front, such as a coal furnace, it is very difficult to obtain agreement over the rows. With a high muffle draft, all cupellations have an over abundance of oxygen; there will be little difference in time of cupellation between front and back. The rear ones usually have the higher losses, due to several reasons. The rear muffle temperature is higher to begin with, and this is augmented by the heat of oxidation of all the cupels in front. If, on the other hand, the air rate is low, and by the time it has reached the rear only sufficient oxygen is available to keep the rear cupels open under slow oxidation, the loss conditions will be different. The proper balance may be struck, and fairly even losses be obtained throughout. The back cupels, though in the hottest part of the muffle, have a low lead surface temperature. The significance of this temperature is shown in Part V. They may be longer in cupelling than the front cupels under fresh air supply and its cooling effect, but may give similar losses.

In a gas muffle with a row of taps, the flame from front to rear may be adjusted to give any desired graduation of temperature. With a muffle full of cupellations, the air supply and relative temperature throughout the muffle may be adjusted so that the lead surface temperatures of all the rows, from front to rear, are practically alike. It will be an aid in promoting uniform air supply, to admit it, near the muffle roof above a high door. Under these conditions the times of cupellation and losses, over the entire muffle floor, will be fairly

uniform. These are the ideal conditions to strive for, requiring as they do a nice sense of compromise, they are not always easy to obtain.

In a great deal of routine assaying, it is probably a matter of little consequence whether the loss is, say, 1.5% or 2.5% or higher, so long as it does not vary unduly; the error in assaying may be of no consequence compared to other errors, as in the preparation and selection of the sample from the ore body or process the sample represents. There is a loss always, for which allowance can be made, if necessary by running checks. To mean much these must be run under conditions as identical as possible with those they purport to check. Close attention to air supply will give greater uniformity in the losses; if this attention is neglected in every day work, it will likewise be neglected when more careful work is attempted, for familiarity breeds contempt in assaying as well as elsewhere. It behoves the operator to study his draft and muffle conditions, if he is to do consistent work. Outside of actual heat input to the muffle from the heat source, and of impurities in the buttons, there is no other variable having so potent an effect on loss as air supply.

PART III.

PURPOSE AND SCOPE OF THE WORK.

In this part the primary intention was to obtain a relation between loss, and the temperature of the air passing near a cupellation. As a result of this work, considerable information pertaining to opening and finishing temperatures, freezing, litharge pools, and slag bottoms was obtained.

APPARATUS USED AND EXPERIMENTAL CONDITIONS.

In Part II the twin muffles were used, and while for part of the experiments here described, these would have served, it was thought better to change the furnace, so that all the planned work at the time could be performed with the same set-up, still retaining a rigid air control.

Type of Door Used.

The door used here is shown in place in Fig. 1 on the furnace, in Fig. 17(a), also in plan and elevation in Fig. 17 (b). It fitted tightly into the muffle opening; the joints were filled with alundum cement. It was made up of asbestos plates of half inch thickness. The door was hinged at the bottom, and was held tightly closed during operations by a wing nut. The peep hole or window was made of sheet iron,

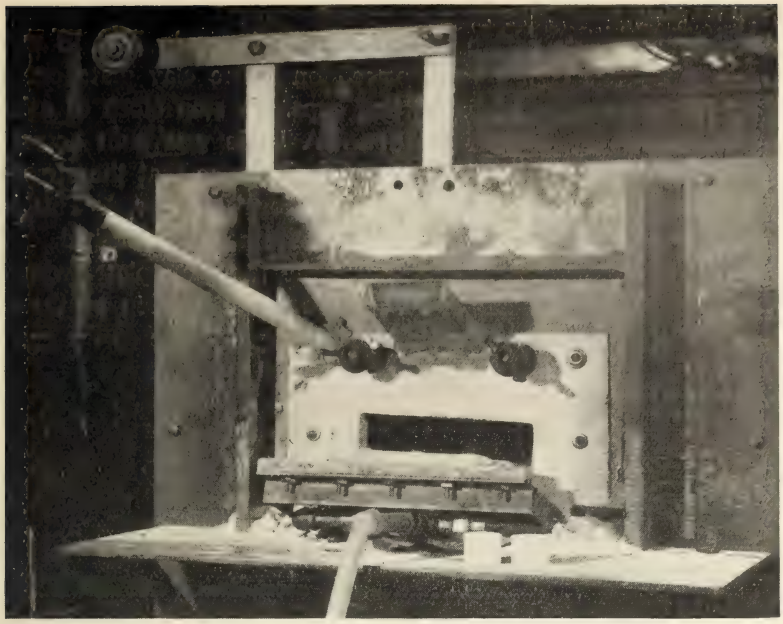


Fig. 17 (a).

with flanged joints, and had a glass $\frac{3}{4}'' \times 3\frac{1}{2}''$ in front, through which the progress of cupellations within the muffle could be observed. The air distribution pipe was made of $\frac{1}{2}$ and $\frac{3}{4}$ inch diameter; the pipe facing the door was drilled with an $\frac{1}{8}''$ drill, with holes in two rows, spaced at $\frac{3}{8}''$ centres.

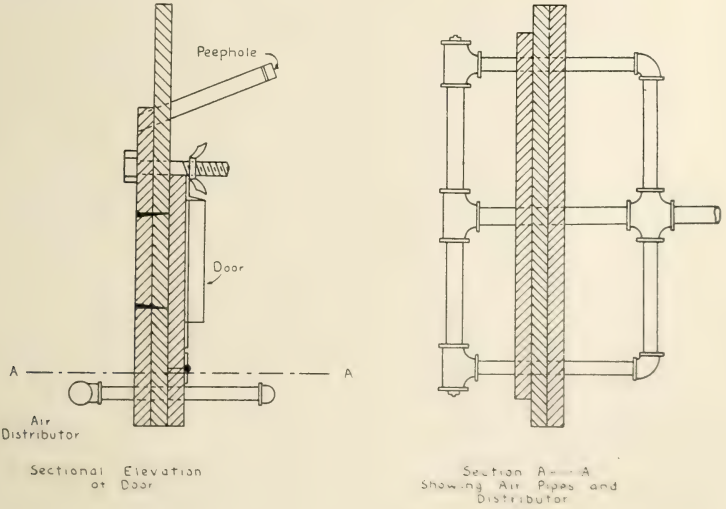


Fig. 17 (b).

Interior of Muffle.

The arrangements within the muffle are shown in Fig. 18 in plan and elevation. The cupels were placed on a fire clay plate one inch thick, which was supported on parting cups. A stop block of asbestos behind the cupels fixed their position. A baffle was built across the fire clay plate and in front of the cupel position, so that the air supply would pass over the cupels in a fairly uniform manner. This baffle was formed of alundum cement, and was smoothly finished. The furnace thermocouple was placed under the fire clay plate, where, in close proximity to the muffle floor, it gave prompt action of the automatic control in response to temperature changes. Due to the confined

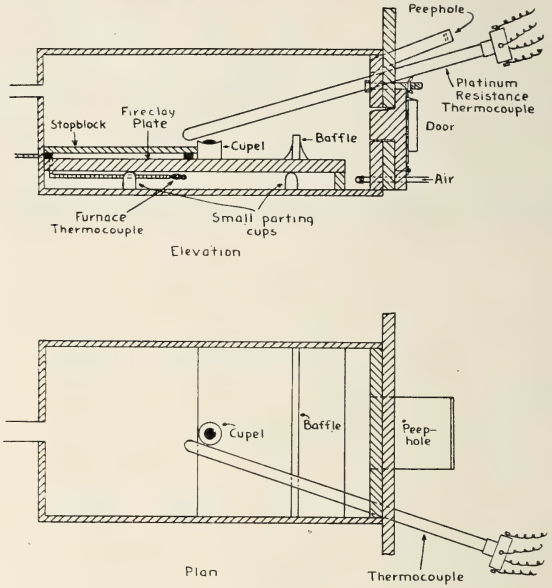


Fig. 18.

position of the furnace couple, it was necessary to operate the automatic control at considerably higher temperatures than those shown near the cupels, above the intervening fire clay plate. A quartz protecting tube for the Platinum resistance couple was luted in a fixed position in the door frame. An alundum cement luting protected it against litharge fumes. For temperature measurements a Cambridge Whipple indicator was used. This could be read to 1° C., although it indicated smaller temperature changes. It was checked against room temperature, as well as the melting points of lead, sodium chloride and copper. With these it was in good agreement. The couple end of the tube was placed above, behind, and to one side of the central cupel

about one inch from its upper edge. The difference in temperature between this position and that of the central cupel for a range of from 850 to 950° C. was not more than two degrees, with air passing through the muffle as in the experiment to follow. For air supplied up to 15 litres per minute, measurements were made with the Precision Meter. For higher amounts a government tested dry gas meter was used. This was in satisfactory agreement with the Precision instrument within the range of the latter. The air supply pressure was fairly constant, differences of about 2% occurring throughout the day.

A—Average Air Temperatures and Loss.

In Part II, temperature was held practically constant, and air was varied. Here the reverse holds; air conditions were kept alike in the trials, while temperature was changed from run to run. Air was passed to the muffle at a rate of 6 litres per minute. The cupels were placed in position with the air on, the door was closed, and at least 10 minutes allowed for heating of the cupels. After this period, when the power was cut off and the blue light exitnguished, the buttons were inserted. The door again was closed. The cupellation was timed from its opening, to the play of colors. Temperature readings were taken every minute, starting one minute after opening, and continued to one minute after the blick. All points of interest, such as temperatures where feathers form and melt, buttons open or freeze, were observed and noted. This procedure and set-up was used for most of Part III; where conditions other than these were employed, they are mentioned with the tests to which they refer.

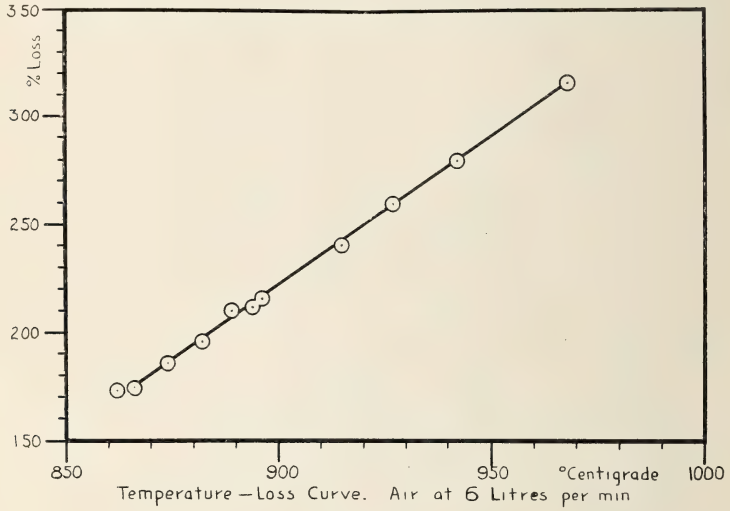
Cupellations were here opened at about 900° C., and where average temperatures below this were required, the power was cut out by the hand switch. For the balance of such experiments control was either by hand or automatic, as seemed best to give the desired conditions. For temperatures over 900° C. the automatic control was utilized; here opening took place near the average temperature of the whole run.

The Results of the Air Temperature Experiments.

It is with some diffidence that the average temperatures here are referred to as air temperatures. Air temperatures so taken are a compromise of many factors. Among these may be mentioned: the conditions of set-up; the location of the couple relative to the cupellation, and to the muffle boundaries; the air supply, the lag of the couple. There may be other dominant factors. The indicated measurements vary at

different locations, and serve merely as a yard stick to compare the runs here among themselves. With the work of others, they serve only to compare by analogy, unless the set-up is duplicated.

The results of experiments ranging in average temperatures of from 862—968° C. are given in Table 18. Included are some results from work on slag buttons from scorification fusions of lead borax and silica, to be described more fully later. In experiments 1-2-3 these buttons were alongside those made up of pure lead and silver. Note that the extra cupellations present, prolonged the time for the regular

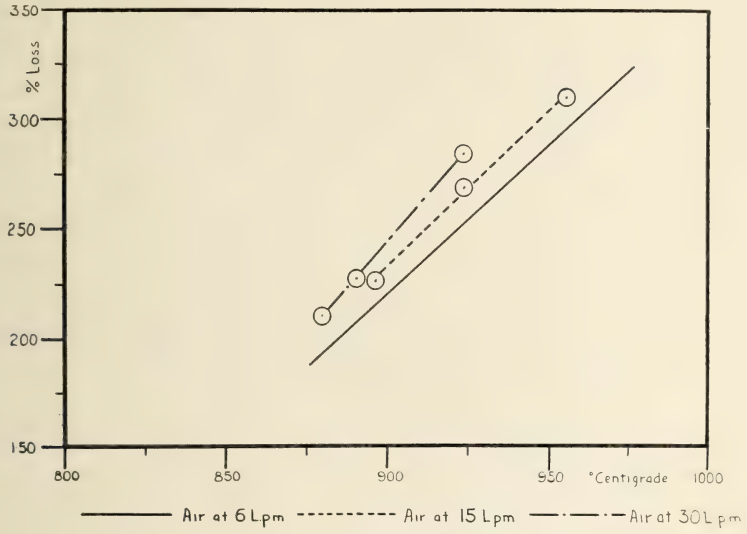


Curve 9.

TABLE 18. AIR AT 6 LITRES PER MINUTE. TEMPERATURES VARIED.

Exp.	No.	Time min.	Average Temp. Deg. C.	Finishing Temp. Deg. C.	Loss %	Remarks.
1	(a)	21½	862	893	1.73	Feathers melted 888 Deg. C.
1	(b)	23	866	865	1.74	Slag Button
2	(a)	21¼	874	873	1.86	Slight Feathers
2	(b)	23½	882	879	1.96	Slag Button
3	(a)	21¾	889	886	2.10	No feathers
3	(b)	23	894	897	2.12	Slag Button
4		21¾	896	896	2.16	
5		21¾	915	907	2.40	
6		21¾	927	928	2.59	
7		21½	942	948	2.79	Bead remained molten.
8		22½	968	968	3.16	Bead blicked after removal.

ones somewhat, due to the increase in the oxygen used from the constant air supply. Curve 9 is plotted from Table 18. It is a straight line, *i.e.*, air being a constant, loss varied directly with air temperature within this range. Furthermore, since the cupellation time for a range of over 100° C. variations is practically the same in all cases, it is concluded that this time is not affected to any noticeable extent by temperature. Throughout all of Part II, where temperature was constant, the time of cupellation decreased definitely, and greatly with increase in air supply. It is concluded then that air supply to a cupellation is the main controlling factor affecting time of cupellation.



Curve 10.

As a confirmation of the previous results, a few experiments under the same conditions as for Table 18 were run at higher air supplies, fifteen and thirty litres of air per minute. Only three cupellations at each rate were made, these alone being sufficient to establish the

TABLE 19. AIR AT 15 & 30 LITRES PER MINUTE. TEMPERATURES VARIED.

Exp. No.	Air in Litres per min.	Average Temp. Deg. C.	Time Min.	Loss %
1	15	896	20	2.27
2	15	923	20¼	2.63
3	15	955	19¾	3.09
4	30	880	19½	2.11
5	30	890	19½	2.28
6	30	923	19	2.84

straight line relation between temperature and loss. This information is in Table 19, and is plotted in Curve 10. Observe the parallelism of the lines, the decrease in cupelling times at these higher air supplies, and the increase in loss.

THE OPENING TEMPERATURES OF BUTTONS.

The observations to be here given were made for the most part in the preceding work, but to avoid confusion they are separated from it. The objects were:—

(1) To tie in the temperature actually existing in the cupel with that recorded by the thermocouple, and thus have it for future reference. That is, if it was found, for instance, that here in the electric muffle, a button opened at a minimum of say 879° C., then we might be able in another furnace to so adjust a cupel and couple that a similar button would just open at that temperature where the thermocouple recorded it. Then the two set-ups would be comparable. Owing to the many variable factors affecting the thermocouple reading, as mentioned previously, it was found that this was impracticable.

(2) To determine the melting point of litharge.

(3) To ascertain if buttons resulting from crucible or scorification fusions, would open at lower temperatures than those made from sheet lead.

The tests on slag buttons were made on those from blank scorifications using lead and borax, and weighing within 0.1g. of 15g. These were split half way through, and the silver was inserted. The cone shaped button was then hammered into a rough cube, bits of slag still adhered to them. No brushing was done. They were cupelled singly, beside a standard button used in Table 18. The time interval between charging the two buttons was small, probably not over 25 seconds. The slag buttons were charged first.

Experiment 1—(a) (b) of Table 18.

Feathers were formed during the cupellation, and as the temperature was raised towards the end, the feathers were observed to be readily absorbed or melt at 888° C. The standard button opened slowly at 879° C., the slag button 30 seconds later at the same temperature.

Experiment 2—(a) (b).

Both buttons opened at 882° C., the slag button 30 seconds after the standard.

Experiment 3—(a) (b).

Both buttons opened at 891° C., the slag button 5 seconds after the standard.

Experiment 9. Not in Table 18.

A standard and a slag button were placed in well heated cupels at 860° C. This temperature was slowly increased, and considerable oxide formed on the buttons. The slag button opened very slowly at 886° C., the standard one at 893° C.

Some Temperatures Noted.

Buttons open at a minimum temperature of 879° C. Feathers are absorbed at 888° C. Feathers start to form quickly at 825° C. with a low air supply of 6 litres per minute. Feathers form slowly at a temperature as high as 845° C. Above 915° C. beads remain molten for some time after lead has been expelled. A pasty ring or pool of litharge about a button is not absorbed quickly until 894° C. is reached.

The above work shows that:—

(1) A slag button does not open more readily than one of sheet lead, if placed in a cupel when the temperature is high enough to open either of them, viz., 879° C.

(2) Buttons allowed to melt in a muffle too cold require a higher temperature to eventually open them, on account of the heavy oxide coating which forms.

B—FINISHING TEMPERATURES, LITHARGE POOLS AND FROZEN BUTTONS.

The points here investigated were:—

(1) *Finishing Temperatures.*

At what temperature of finishing will a bead retain lead, when cupelled in a standard bone ash cupel?

(2) *Litharge Pools and Frozen Buttons.*

(a) What is the loss on beads finishing in a pool of litharge?

(b) What is the loss on frozen buttons, which are reopened and finished?

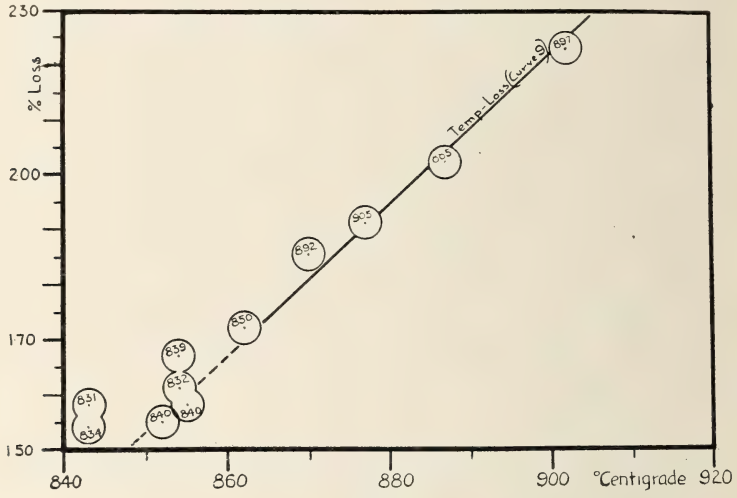
(c) What is the loss when dry litharge flux is added to molten silver?

(1) FINISHING TEMPERATURES.

These experiments were performed under the same general conditions as A. The results are gathered in Table 20.

In Curve 11, the temperature loss curve at 6 litres of air (Table

18, Curve 9), is plotted as a heavy straight line. Table 20 results are also shown located on a basis of average temperature. The figures at each of these points indicate the air temperature at which that particular cupellation finished. Now, if these were below the heavy line, it would show an indicated lower loss, and that probably lead had been retained. Falling near the line would indicate the absence of lead. The first four results were from cupellations comparable with those of Table 18, *i.e.*, finished near to 900° C.; the remainder were completed at much lower temperatures. Only those cupellations which finished with a normal play of colors, brightening and blick, are considered here in Table 20 and its Curve 11.



Curve 11.

TABLE 20. LOW FINISHING TEMPERATURES. AIR AT 6 LITRES PER MINUTE.

Exp. No.	Time Min.	Average temp. °C.	Finish temp. °C.	Loss %	Remarks.
1	21¾	887	885	2.02	Run to tie in with curve 9.
2	21¾	902	987	2.23	Ditto.
3	22¼	877	905	1.91	Ditto.
4	22½	870	892	1.85	Ditto, (slight feathers).
5	22¾	862	850	1.72	Good feathers.
6	22¼	855	840	1.58	Ditto.
7	22¾	854	839	1.67	Ditto.
8	22¼	854	832	1.61	Ditto.
9	22¼	843	834	1.54	Ditto.
10	22½	843	831	1.58	Ditto.
11	22¼	852	840	1.55	Ditto.

Interpretations of Curve 11.

Beads finished in standard bone ash cupels at the temperatures recorded above do not contain lead, save in so far that all beads probably retain traces. The straight line may be continued down to a point with these low finishing temperatures, where the button froze or formed pools of litharge, *i.e.,* if considered as beads they finished with lead. The line does not curve downwards to give a zero loss or a positive surcharge due to lead retention. The interpretation of this work, then, is that with a low air supply and a cupel protected from cold draughts, cupellations in bone ash cupels need not be raised unduly in temperature at the finish to expel lead.

(2) LITHARGE POOLS AND FROZEN BUTTONS.

(a) *Beads finished in a pool of unabsorbed litharge.*

In obtaining the preceding results, many buttons froze or did not reach a normal satisfactory finish. These are now described to illustrate how freezing and insufficient absorption of litharge affect the silver loss.

Test 1.

The button was opened at 889° C., which was lowered to 802° C. where feathers were forming rapidly. The power was put on, and the temperature raised. At 835° C. a pool of pasty litharge formed around the cupelling button; the bead gave evidence of finishing in this about one minute later at 840° C. By the time the cupel could be removed the litharge had been absorbed, leaving the usual glazed surface, where it had been in contact with the cupel surface.

The bead was flat, and but slightly attached to the cupel. It had a dull glazed appearance. On being cleaned, very thin yellow scales, obviously litharge, brushed off.

The cupelling time was 22 minutes and the loss 2.43%. This is about 0.9% high for this temperature.

Test 2.

The button opened at 877° C., and the temperature was dropped to about 810° C., where it was held until the end of the drive. The cupellation time was 22 minutes. At 21 minutes the litharge pool came inside of heavy feathers as in Test 1. The bead finished with a play of colors and blicked weakly. The glaze on the cupel was present, but no scales on the bead. The loss was 2.63%, or about 1% high for this temperature.

Test 3.

Here uncovering occurred at 879° C.; the temperature was lowered to 789° C., where the button froze when the total time of cupellation was 18 minutes. The litharge pool was absent, but there were very heavy feathers. The temperature was increased to 894° C.; the button opened in a pool of litharge, the feathers having melted. It finished then in four minutes, making the total time it was open 22 minutes. The loss was 2.35%.

Test 4.

This cupellation opened at 880° C.; the temperature was lowered to 816° C., where it froze ten minutes later. The temperature was raised; the bead finished after the litharge was absorbed at 898° C., the temperature at the finish being 910° C. The bead was attached, flat, and had a glassy appearance. Scales were detached on cleaning. The loss was 7.21%.

2 (b). Frozen Buttons Recupelled with Added Lead.

Test 5.

Opening occurred at 882° C., the temperature was reduced to 814° C., then raised to 848°, where a pasty ring had formed. This apparently finished, partly covered by the ring at 862° C. Two grams of sheet lead were added, the temperature was increased, and the cupellation reopened in the pasty litharge ring in four minutes. At 894° C. the ring was absorbed, and the bead finished to all appearances, normally. The loss was 12.10%.

Test 6.

After the litharge ring appeared and freezing occurred, two grams of sheet lead were added, as before. When the litharge ring again appeared, two more grams of lead were added. This finished normally with a 7.82% loss or 4.28% less than Test 5.

Test 7.

A button opened at 880° C. was lowered to 779° C., where it froze. Time 22 minutes. The temperature was increased and ten grams of lead added. It opened at 880° C., but no litharge pool appeared. It finished at 890° C. with a loss of 2.94%.

2 (c). Litharge in Contact with Silver.

As a further contribution to the effect of litharge on the loss of silver, the results of some work performed in a wire wound resistance

furnace will be described. The purpose of these experiments was to determine the loss of silver while in contact with litharge, such as is used as a flux in crucible assaying. Some startling losses were obtained, and as the work throws new light on this phase of cupellation, it is here described. An alundum tube 24 inches long and 2 inches inside diameter was wound in the central section with nichrome wire. A removable iron cap served as a cover to the tube. This had an inlet pipe for air and a glass window at its centre through which operations within could be watched. The base of the alundum tube was closed; it was provided with exit pipes for fumes to pass out of the tube. Through the centre of this base, the quartz protecting tube of the Cambridge Pyrometer passed upwards, to about the centre of the alundum tube. The quartz tube was alundum coated, and the upper end was finished flat on top, so that a cupel could be supported on it. The pyrometer tube was adjusted to a position where with a bone ash cupel on it, and containing silver; the latter would melt when the instrument indicated 962° C. The current utilized was 110 volts, with rheostat control.

In this work, air at 1 litre per minute was passed through the furnace, merely to sweep out any fumes which might have a tendency to arise and cloud the observation window. About 100 milligrams of silver were used in each test.

Test 1.

Furnace at 900° C. Ten grams of dry litharge were placed on top of the silver on an inch and a quarter diameter bone ash cupel, which had previously been heated in the furnace. The cupel was placed on the upper end of the pyrometer tube in the furnace at 900° C. In about 7 minutes the litharge had sunk into the cupel. The silver gained in weight by 1.67%, due to slight incrustations on the surface from the litharge.

Test 2.

Furnace at 965° C. to 970° C. Ten grams of litharge were placed on the cupel, and on top the silver in one flat piece. The litharge was observed to form into a pasty semi-fluid mass; it sank into the cupel inside of five minutes. The silver softened at the edges and rolled into a sphere on the cupel, when the litharge had all soaked away. No fumes were visible. Around the silver was a distinct dark green stain so characteristic of high loss throughout this research. The silver loss was 32.8%. The cupel was assayed, and 30.87% of the original silver was recovered.

Test 3.

This was a repetition of 2, save that the silver in three small pieces was placed under the litharge. When the litharge disappeared, one piece of silver had melted; the other two were melted a half minute later. The loss was 15.57%; the cupel recovery was 14.38% of the original silver. The green stain appeared under each of the pieces of silver, but not as dark in color as in 2.

Test 4.

Quite similar to previous tests, except that the silver was cut into ten fine thread-like pieces, and placed on the litharge, but appeared as beads all over the cupel later. Each was surrounded by the characteristic green stain accompanying high silver losses. The loss here was 16.59% of the silver; the recovery from the cupel amounted to 15.67% of the original silver.

Test 5.

One gram of sheet lead was rolled very thin, and in it was wrapped 10 grams of litharge. The silver was melted on the cupel at 970° C., and on it was placed the lead packet. The lead formed two globules, on opposite sides of the cupel, beside the litharge. These cupelled during the last of the run, and when all the litharge was absorbed coalesced with the silver. This then finished like an ordinary bead. The furnace was slowly cooled to avoid sprouting. The loss was 5.01%. Here the lead protected the silver from the heavy losses of over 15 to 30% which previously occurred with no lead present. Doubtless the litharge was responsible for considerable of the loss, however, as it is high for a cupellation even at this temperature when only one gram of lead is used, a short cupellation. Most assayers have likely observed that if a cupellation freezes about midway or before, and is reopened by raising the heat, that the increase in loss due to freezing or litharge contact is not as heavy as when freezing occurs near the end, when the amount of lead is quite low. This, it would appear, is due to the protective effect of the larger amount of lead present in the former case. The lowering of the heavy losses in Test 5 assuredly was due to the lead present.

As a further verification of these high losses due to litharge, another operator did four charges, in a gas muffle furnace, using 10 grams of litharge and about 100 milligrams of silver in each case. These were arranged as follows:—

(1) Silver on cupel—litharge on top.

(2) Three grams of litharge on cupel, silver on this, and 7 grams of litharge on top.

(3) Seven grams of litharge on cupel, then the silver, and three grams of litharge on top.

(4) The silver on top of the litharge.

The muffle was at 1000° C. when the cupels were charged, but dropped to about 950° C. during the charging, and when all the litharge was absorbed in about three minutes, the silver melted on the cupels at about 970° C.

The losses were:—

(1) 5.55%
(2) 13.37%
(3) 29.82%
(4) 23.16%

This would indicate that No. 3, with litharge above the silver and below it for a longer period than the others, gave the highest loss due to this long contact with litharge. Further experimentation with this litharge effect, under more favorable control, may be undertaken in the Hoskins Electric Muffle Furnace.

SUMMARY OF B2. (a), (b) and (c).

(1) The formation of a litharge pool about a button gives high losses.
(2) If a bead finishes in a pool, the loss may appear to be only moderately high, due to the presence of retained lead, which in part compensates for the really high silver loss.
(3) If the frozen button is re-cupelled with a small amount of lead, the bead will finish as silver, but will give a high loss.
(4) If the frozen button is re-cupelled with a large amount of lead, the loss will only be moderately high. The lead added reclaims much of the silver, which had passed to the litharge.
(5) Litharge alone gives extremely high loss with silver.
(6) Lead protects the silver from loss to the litharge.
(7) Discard all frozen buttons.

PART IV.

THE INFLUENCE OF AMOUNT OF LEAD PRESENT ON SILVER LOSS.

It has come to the writer's attention, on visiting many assay offices, that at times very little attention is paid in some, to the weight of buttons obtained from an ore fusion. It is true, that at times this is a difficult matter to control, where htere is a wide range of reducing power in the samples received. If the weight of buttons is allowed to vary from practically nothing up to the capacity of the cupel, and maybe more, it is an evidence of indifference, or carelessness, and the results

will show it. It is a very universal flux indeed, that will function properly with these wide variations in lead fall. With the small buttons there is danger of not collecting all the values; with the largest ones the cupel is overloaded, giving slow absorption at saturation, and probably causing mechanical losses due to spillage. This is aside from the differences of loss in cupelling, due to the fact that the cupelling loss increases with the amount of lead present.

To show the effect on loss caused by using different amounts of lead, and as well the effect of using cupels of different size with these, two series were run. With one series, inch and a quarter diameter cupels were used; with the other they were inch and a half. These were made with Ihler moulds. The cupels were placed in a row across the Hoskins muffle, one cupel for each weight of lead used with 100 milligrams of silver. Enough runs were made in each series so that each weight of lead used, occupied in turn each position across the row once. At the ends of the row, dummy cupellations were run on 16 grams of lead, in order that the end cupellations should not receive a higher air supply than the central ones while all were cupelling. Air was supplied at 3 litres per minute, and temperatures taken as in the preceding work. The results are set forth in Tables 21-22.

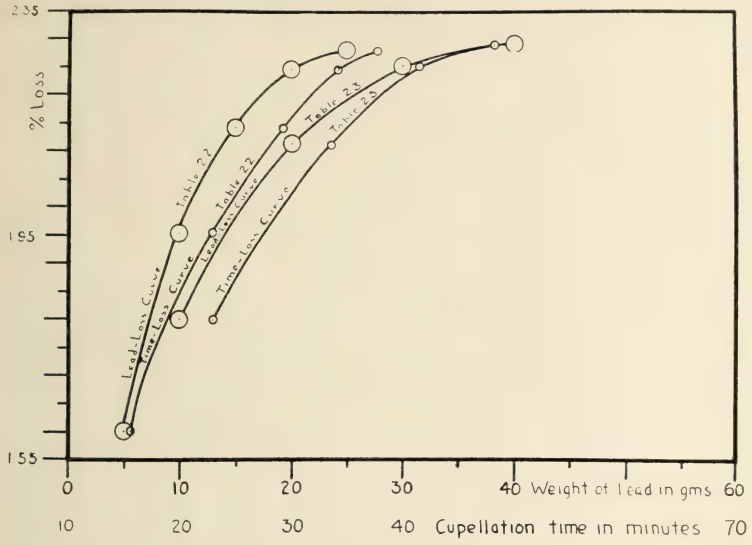
TABLE 21. EFFECT OF LEAD ON SILVER LOSS—CUPELS 1.25 INCHES IN DIAMETER.

Exp. No.	Temp. Deg. C.	Lead 5 g Loss%	Lead 10 g Loss %	Lead 15 g Loss %	Lead 20 g Loss %	Lead 25 g Loss %
1	900	1.61	1.98	2.18	2.23	2.30
2	901	1.65	2.05	2.19	2.25	2.31
3	899	1.61	1.97	2.15	2.18	2.27
4	899	1.57	1.93	2.10	2.19	2.27
5	898	1.56	1.82	2.08	2.15	2.25
Average Loss		1.60	1.95	2.14	2.24	2.28
Average Time, mins.		15½	23	29¼	34¼	37¾

TABLE 22. EFFECT OF LEAD ON SILVER LOSS—CUPELS 1.5 INCHES IN DIAMETER.

Exp. No.	Temp. Deg. C.	Lead 10 g Loss %	Lead 20 g Loss %	Lead 30 g Loss %	Lead 40 g Loss %
1	899	1.85	2.10	2.26	2.35
2	900	1.78	2.09	2.27	2.30
3	900	1.78	2.14	2.21	2.30
4	900	1.83	2.10	2.22	2.29
Average Loss		1.80	2.11	2.25	2.29
Average Time, mins.		23	33½	41½	48¼

On Curve 12, the silver loss has been plotted against both lead and time of cupellation. Observe that the larger cupels give lower losses for the same weight of lead than the smaller, and require more time. In our work increased time of cupellation generally indicated a lower loss. These cupels have the same depth of cup. This should be remembered in interpreting the results, and also that in either cupel a small amount of lead has more protection than a large amount. The author is inclined to believe that this protection affects loss here, as has been illustrated in the hood and ring experiments of Part II. That the loss



Curve 12.

would increase with the lead was anticipated, but that the wider cupels would give a lower loss was not. Aside from the advantage of eliminating the danger of spillage, and the increased loss due to over saturation by using cupels that are too small, it would appear to be good practice to use cupels of oversize, where low losses are desired.

INFLUENCE OF AMOUNT OF SILVER PRESENT ON LOSS.

This phase of cupellation has received considerable attention, and many data are given in the literature. Among others the work of "Eager and Welch", (r) "Godshall" (s) and "Kauffman" (t) may be mentioned. These are quoted in various text books on Assaying. The

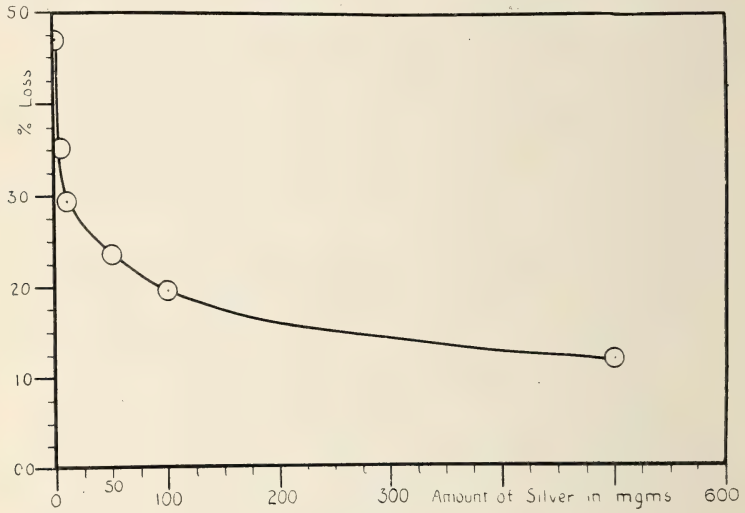
(r) J. Eager & W. Welch in Lodge's "Notes on Assaying".
(s) L. D. Godshall. Trans. A.I.M.E. XXVI, 473.
(t) Kauffman. E. & M. J. LXXIII, 829.

operators mentioned cupelled at low temperatures of air in the muffle such as 750° C., to obtain very low losses under feather conditions.

The agreement between these operators is good, when it is considered that the temperatures are estimated, and there is no statement regarding draft save that feathers were obtained.

TABLE 23. % LOSSES ON VARIOUS WEIGHTS OF SILVER.

Exp. No.	Temp. Deg. C.	1 mg.	5 mgs.	10 mgs.	50 mgs.	100 mgs.	500 mgs.
1	898	5.0	3.89	2.92	2.40	2.00	1.23
2	895	4.5	3.39	2.95	2.32	1.93	1.20
3	894	4.45	3.63	2.83	2.38	1.96	1.17
4	899	5.10	3.75	3.31	2.47	2.04	1.23
5	885	4.30	3.15	2.47		1.76	1.11
6	892	4.75	3.29	2.92	2.34	1.95	1.14
Average loss		4.70	3.52	2.90	2.38	1.94	1.18



Curve 13.

In the tests here made for the effect of silver on loss, 1¼ inch standard bone ash cupels were used, with 15 grams of lead, and silver varying in amount from 1 to 500 milligrams. Air at 3 litres per minute was utilized. The tests were made with a closed muffle door.

Much lower losses would, of course, have been obtained if the temperatures had been dropped after the opening and maintained low through the drive. The intention here, however, was to keep the air, the temperature and other variables as constant as possible, and compare on the basis of silver only varying. The cupellations were run one row

at a time, and as with the lead experiments just described, each weight of silver used was moved to a new position with each successive run until all positions had been occupied. In this way variations in loss due to position in the row would be minimized, when the average is considered. The results of these runs are presented in Table 23 and are plotted in Curve 13. The percentage loss decreases rapidly with increase in silver present. The losses here agree very well in magnitude with those of the authors quoted, where a much lower air temperature was utilized, and probably a very much higher air supply. Losses observed by Kauffman when 15 grams of lead were used and bone ash cupels, may be found in C. Fulton's "Manual of Fire Assaying". In E. Bugbee's "Text Book on Fire Assaying" representative figures from Godshall's paper are given.

PART V.

A Study of Litharge Surface Temperatures.

As pointed out by Dewey (u), "the temperature that controls the results and success of a cupellation is the temperature of the cupelling lead button," but, as he states, "there is no method available for determining this temperature." There are mechanical and other difficulties in measuring its temperature, due to failure of couple protective tubes when immersed in it. Bannister and Stanley (v) took temperatures of the alloy during the first six minutes of cupellation, while investigating the thermal properties of Bone Ash and Morganite cupels, when the protective tubes failed. Fulton (w), with a couple in a cupel and just under the alloy, obtained temperatures closely related to it, and shows comparisons of these with those of muffle air and blank cupels. No information has been found in the literature connecting the alloy temperatures so obtained with loss. Even if a couple would withstand the effect of the corrosive oxides on it, throughout a cupellation, there would come a time at the end, when most of the lead was oxidized (near the bead stage), when the alloy would likely break up into separate globules, due to the presence of the couple, so that correct temperatures could not be obtained right to the end, and, further, the cupellation would not then have a normal ending.

The alloy receives its heat supply in two main ways: (1) From

(u) Dewey, F. P.—"Bone Ash Cupels". T.A.I.M.E. Vol. IIX, 1918.

(v) Bannister & Stanley—"Cupellation Experiments; The Thermal Properties of Cupels". T.I.M.M. Vol. 18, 1908-9.

(w) Fulton, C. E. & M. J. Vol. 86, 1908.

the source of muffle heat, mainly from beneath through the cupel, to a lesser degree from above, by radiation from the walls. (2) From the heat of oxidation to litharge at its surface.

During cupellation the heat generated at the surface, passes in part to the cupel through the alloy and with the absorbed oxides. Much of the heat is dissipated to the air surrounding the cupel, and this greatly affects any couple held near by. It is likely that the alloy is in temperature (once active oxidation begins), between that of the surface litharge and that of the cupel just under the alloy.

Close view of a cupellation, with 100 milligrams of silver present, shows bright patches of litharge floating on a darker background. This is more apparent if buttons containing several grams of silver be cupelled (5 grams for instance), and appears earlier in the process then. Viewed from above, the litharge film rises from the cooler side of the cupel, and passes across to the hotter side, at first entire, but later breaking up into small floating islands. These are always much brighter in color than the lake of alloy beneath, and increase in size with the amount of silver present. If a cupellation in active progress be quickly checked, by stopping the oxidizing draft through the muffle, and forcing the reducing furnace gases instead back over the cupels, the brightness at the surface quickly goes when oxidation ceases, and before the alloy as a whole would have time to cool. Then the surface is dull, by comparison, with the previous brightness—indirect evidence that the film is hotter than the alloy.

These surface film temperatures can be measured by an optical pyrometer, with an approximate degree of accuracy, and with which relations with loss may be established. As these temperatures are closely related with that of the alloy, and the film is in view of the operator throughout, any information found should be of interest and usefulness.

It is shown in "Pyrometric Practice" (x) that these optical temperatures are in error, if viewed through intervening glass, if non-black body conditions exist within the furnace, or if smoke intervenes. All these conditions introducing error were present to some degree in this work, but to use a statement from the above reference, "the observed temperatures, although known to be low, will be low by the same amount from time to time, and hence will serve just as satisfactorily for reproducing temperature conditions in any process as the corrected temperatures." Towards the end of all cupellations, there is normally a rapid rise in surface temperature, hence optical readings must be quickly taken, on the fly as it were, without opportunity to check them. At this stage the button is small; it requires practice to focus the pyrometer on it with certainty. In short cupellations where few readings

may be taken, these later mentioned troubles introduce greater error in the average readings than in long ones, where many readings are obtained.

PREVIOUS WORK UTILIZING SURFACE LITHARGE TEMPERATURES.

Apparatus Used.

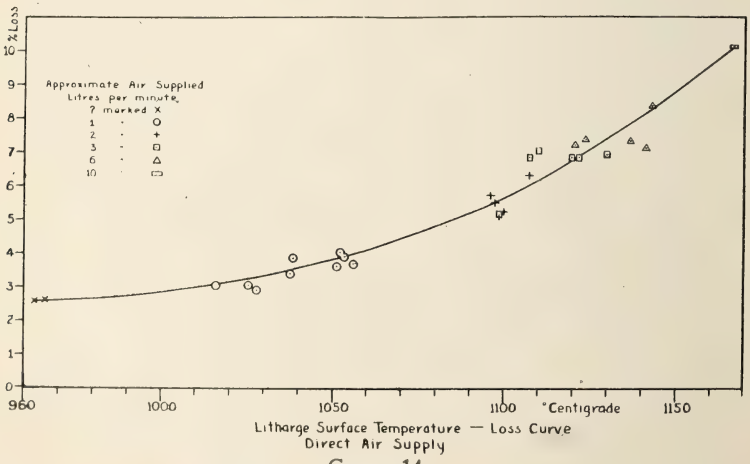
In the twin muffle work of Part II, it was intended to observe these temperatures throughout, but unforeseen mechanical difficulties made this impracticable. The observation tubes were not at sufficient angle to the cupels to observe the finishing temperatures, and owing to the smallness of the diameter of the tubes, 5/8", and their length (12"), it was extremely difficult and tedious to focus the lamp filament against the glowing button. In the previous year, however, using a wire wound electric muffle of the same size as the twin muffles, with a vertical observation tube directly above the cupel, and with the objective of the Leeds and Northup disappearing filament type pyrometer, about 8 in. from the cupellation, more satisfactory conditions to measure the surface temperatures existed.

Procedure of Tests.

In that work, two cupels, one a blank, were placed across the central line of the muffle. In the blank a couple was located, and also another 1/4" above. These were connected to a Pyrovolter instrument, and so-called blank and air temperatures were taken. The 100 volt current was hand controlled by a rheostat, and was adjusted to give 930° C. in the blank just before cupellation commenced. Cupels were placed some thirty minutes before this. The button was charged, through the vertical observation tube with a hooked wire. As it was thus not necessary to open the muffle door, the charging caused but little drop in muffle temperature. These temperatures varied somewhat from run to run, due to uncontrollable voltage changes. A direct air supply was used through a 1/2" diameter iron pipe inclined at an angle of 30° to the cupel and ended 1 1/2" from it. The air impinged over the lead surface and top of the cupel. Fifteen gram lead buttons with 100 milligrams of silver were used. Air was supplied through the Precision meter and was read before and after each run. Temperatures were taken each minute and a half. The exit fumes passed from the rear to a vertical pipe 1" in diameter, some 8 ft. in height, exhausting into the room; no chimney or other suction was used. Air from "natural suction" or as drawn by the pipe, up to about 10 litres per minute, were utilized in the series.

TABLE 24.

No.	Litres air per minute.	Minutes to cupel.	Average Temperature °C. Air	Blank	Litharge surface	Silver Loss %
1	Natural suction	30½	915	927	963	1.98
2	„ „	30½	921	930	966	1.98
3	0.96	14	919	927	1017	3.06
4	1.04	12½	913	918	1027	3.09
5	0.92	12	890	906	1029	2.94
6	0.96	11½	921	929	1040	3.92
7	0.99	11½	903	914	1039	3.43
8	1.04	11½	920	929	1055	3.93
9	1.08	11½	910	921	1053	3.63
10	1.06	11½	921	930	1054	4.10
11	0.89	13	928	936	1058	3.72
12	2.04	7½	920	927	1098	5.13
13	1.93	8	920	928	1095	5.73
14	1.97	8	916	923	1096	5.57
15	2.03	7½	912	920	1099	5.28
16	2.03	7½	911	919	1107	6.20
17	2.18	7½	924	930	1098	5.16
18	3.02	6½	927	932	1119	6.70
19	2.96	6	921	926	1107	6.70
20	2.98	6	914	920	1109	6.97
21	3.09	6	917	926	1130	6.84
22	3.31	6	926	928	1121	6.70
23	6.40	4½	917	920	1143	8.28
24	5.66	5	919	923	1120	7.11
25	5.72	5	917	922	1123	7.28
26	5.70	4½	913	921	1136	7.18
27	5.96	5	916	922	1141	7.01
28	9.71	3½	934	941	1167	10.09



Curve 14.

Results of Tests.

The results are given in Table 24. In Curve 14 the average surface temperatures are plotted against their corresponding loss. The approximate rate of air used to obtain each point is indicating by referring the mark used for it to the legend shown.

The aim here was to keep the furnace input heat as constant as possible, and vary loss by varying air. The conditions for observing the optical temperatures were very good here, with the direct view from about 8″ above. In spite of this there is considerable deviation in loss for the same surface litharge temperatures. More readings per run would doubtless have given closer agreement, though this procedure would increase in proportion the number of end readings. These are the most in error, and being quite high, greatly affect the average.

The work shows that increase of air:

(1) Increases the loss of silver.
(2) Increases the litharge surface temperature.
(3) Decreases the time of cupellation.
(4) Gives no definite relation between either its temperature, or that of the blank, and loss.

RECENT WORK UTILIZING SURFACE LITHARGE TEMPERATURES.

In much of the work done with the Hoskins furnace the temperature was under automatic control. The function of the control was to maintain within certain limits a constant temperature. Air admitted to the muffle, in amounts ever so small, would tend to cool it. The effect on the control would be to lengthen the time when power was on, and decrease the time when power was off. In this way theoretically the control would maintain the required temperature in spite of the cooling effect of air, until an amount of air was used which had a greater cooling effect than the heating effect of power on all the time. With the relatively small amounts of air used, preheated in the feed pipes, to a certain extent before entering the muffle, the practical result was that the air in the muffle did not have the cooling effect it would have had—if the heat input from the furnace had been really constant. At the same time, due to some lag in the furnace thermocouple, and opening of the door at the beginning of cupellation, there was a decided drop in air temperature in the early part of all cupellations.

To obtain further information relative to surface litharge temperatures and loss, and under conditions that would allow of the fullest cooling effect of air, a new set-up was arranged for both diffused and

direct air supply tests. With this, and using the 37 volt tap from the transformer, a temperature of about 950° C. could be maintained, when no air was passed through the furnace. The effect of a given amount of air in lowering this temperature was slightly greater in the morning before the furnace body was fully saturated with heat, than in the afternoon. Slight primary voltage changes occurring during the day also had their effect.

DIFFUSED AIR SERIES.

Apparatus Used.

This is shown in Fig. 19. An asbestos door covered the main muffle entrance. Fitted to an opening in the asbestos, and placed inside the main muffle (used as a heating chamber) ½″ above its floor, was a Crystolon muffle of size 4½″ × 3½″ × 10″. The same muffle was used in Part II. For fume exit a horizontal slit ½″ × 4½″ extended across the rear, at 2″ above the floor. The front opening was the

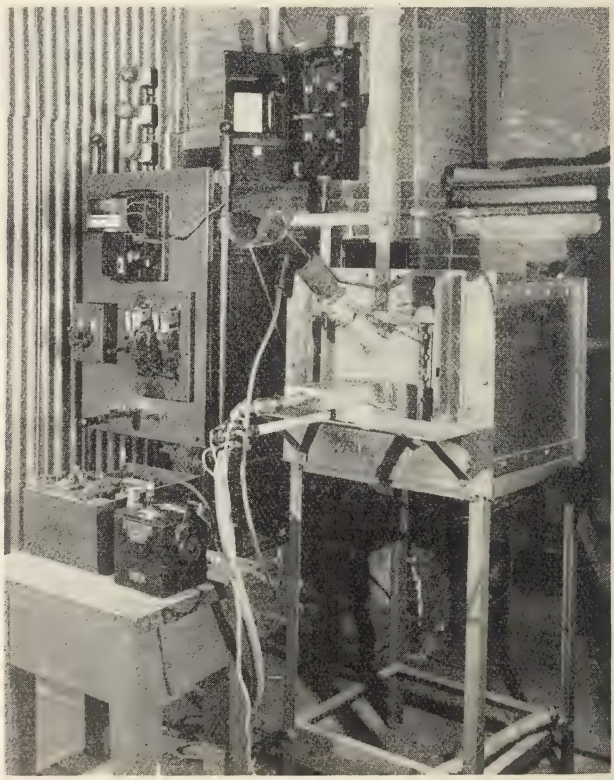


Fig. 19.

width of the muffle, and extended 1¾" below the roof. Air was admitted through a galvanized iron box, one foot long, and closely fitting into the door opening. Air to this was supplied through a 1" diameter pipe from either the Precision Meter or a Standard Meter, the latter for the larger rates of air. Three bone ash cupels (1¼" diameter) were placed 1½" from the muffle rear, and were aligned by a stop block behind. The base metal furnace couple was located ½" behind the small muffle, about 1½" below the fume exit. The Cambridge resistance pyrometer tube was placed an inch in front of the left cupel, below its rim. To more correctly indicate the air temperature, it should have been placed higher and nearer the actual cupellation; then, however, it would have deflected air onto or away from the cupels unduly. The Optical Pyrometer was held in a fixed iron tube, which directed it to the opening of the quartz tube of 1¾" inside diameter. This was inclined at an angle of 45° to the small muffle, and was luted to an opening in the roof. With this diameter and high angle an excellent view of the central cupellation was obtained at all stages. The outer end of the tube was covered by a clear glass plate, held in position by springs. Before making the set up, the base metal and resistance pyrometer ends were placed side by side in the Hoskins muffle. At 950° C. they were in agreement. The Optical Pyrometer sighted on the base metal couple read 6° low.

Procedure of the Tests.

This muffle arrangement was a very fair way of introducing air. The air entrance and exit, across the full width of the muffle, allowed the air to pass in a straight stream line over the cupels, and away. The metal air box prevented side currents and eddies, which would be present to some degree, were the door left open as in ordinary Assaying practice.

Buttons of 15 grams of lead and 100 milligrams of silver were charged to the three cupels, when the main muffle temperature was at 950° C. While buttons were opening, the door was kept closed. The temperature of the air at the resistance tube, of about 890° C., at the charging, would drop from 10 to 20° or more during the opening period. When the drive began, the air box was placed in position. Air in amounts of from ⅛ to 3 cubic feet per minute were used. The temperatures of the three pyrometers were taken at 2 minute intervals.

Results of Tests.

The first set of tests showed that loss increased as litharge surface temperatures decreased, but gave very erratic points when plotted. This

was quite contrary to previous work; this anomalous result was found to be due to slight but progressing fogging of the quartz cover glass, by the litharge fumes.

On repetition of the tests, particular care was taken to clean the glass between runs, and at the higher rate a gentle suction was maintained on the large muffle. The results are given in Table 25. The

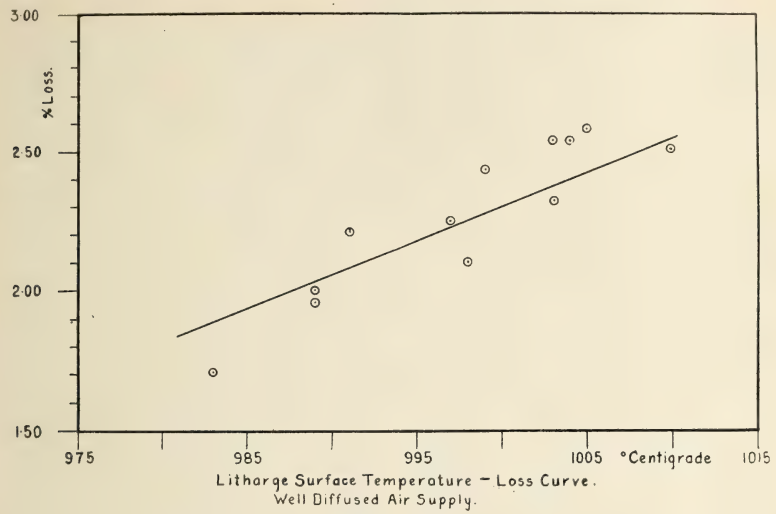
TABLE 25. WELL DIFFUSED AIR.

	Air supply cu. ft. per	Time	Average Temperature °C. Main muffle	Small muffle	Litharge	Loss	
No.	min.	minutes	air	air	surface	%	
1	⅛	23	957	873	1005	2.58	Front stained
2	⅛	22¾	968	872	1004	2.54	„ „
3	¼	22¼	960	867	1010	2.51	„ „
4	¼	22¼	962	865	999	2.44	„ „
5	½	21¾	966	859	1003	2.54	„ „
6	½	21¼	950	847	1003	2.32	„ „
7	1	20¼	950	836	991	2.21	Front not stained
8	1	19¾	943	841	997	2.25	
9	2	18¾	943	827	998	2.10	Cupel noticeably dark
10	2	19¼	923	790	983	1.71	Feathers
11	3	18¼	939	796	989	2.00	„
12	3	18	942	793	989	1.96	„

losses are those of the central cupel. Losses in the right one agreed very closely with this; those of the left one did not. The pyrometer tube, just in front of it, minimized the cooling effect of air, and probably diverted more air to the button. With ⅛ foot of air per minute, the losses in order from left to right were 2.61%, 2.58% and 2.69%. At 3 feet of air per minute, the left cupel loss was 2.69%, whereas the central one gave but 2.00% loss. This illustrates the various cooling effects on the cupels that were present here.

With increase in air supply here, the time of cupellation decreased; thus the heat of oxidation of lead to litharge was liberated more quickly; this of itself would give higher surface litharge temperatures; it would be expected that these would mount. But these were decreased with increase of air, through the variation over the whole range of air supply from ⅛ to 3 feet of air per minute is only 16°. Here, due to the excellent diffusion of air, only a small amount of the total air supplied comes in contact with the alloy, and then at a relatively low velocity as compared to direct air supply. As the air supply is increased, the heat generated on the lead is increased, but here the

cooling effect of air increases in greater proportion. The muffle air is 80° cooler in run 12 at 3 feet of air, than in run 1 with ⅛ foot of air. The optical temperatures from the table are plotted against loss in Curve 15. A straight line has been drawn through the points as representative of the general trend over this short temperature range. The interpretation of this, is that loss increased proportionally with lead surface temperature.



Curve 15.

The resistance pyrometer placed in front of and below the cupellations was probably not greatly influenced by heat liberated at the cupellation, as is ordinarily the case when taken above them. Here, with power from 37 volts, its ability to maintain the general furnace temperature was greatly influenced by the amount of air used. By comparing the temperatures, however, with loss, the trend shows that loss increases as air temperature increases. Here the higher air supplies had a greater effect in cooling the muffle air and the cupel, than in increasing the surface temperatures.

This work shows that increase of air decreases cupellation time, muffle air temperature, litharge surface temperature and loss.

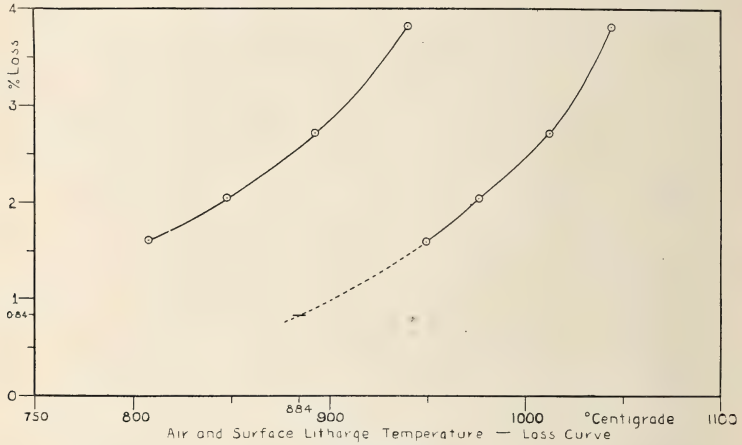
Other points worth noting in these well diffused air runs were:—

(1) Beads were attached.
(2) Blicks occurred in all runs.
(3) With the small muffle air temperature below 850° C. (average), no litharge stain occurred on the cupel fronts.
(4) Feathers formed at air temperatures under 840° C.

Confirmatory Work.

In this work the air supply was kept at 1 cubic foot per minute throughout, while the main muffle temperature was increased from run to run. The results are given in Table 26. In Curve 16 the loss is plotted against both litharge surface, and air temperatures.

The litharge surface temperature curve has been extended down



Curve 16.

to 884° C. (y), by the dotted line, giving an indicated loss at that temperature of 0.84%. The air temperature curve closely resembles the litharge temperature one, in form and direction; the two temperatures follow each other closely here. It is not the straight line reaction found in Part III for air and temperature. Difference in location of the pyrometer couples may in part account for this.

Increase in air temperature decreased the cupellation time. An increase of from 809° C. (No. 1) to 944° C. (No. 4) or 135° C. accompanied a decrease in time of from 21 to 18½ minutes. This decrease was due wholly to air temperature change, as air supply was kept constant. Thus it is seen that air temperature has its effect on

TABLE 26. AIR CONSTANT. TEMPERATURE VARIED.

Average Temperatures °C.

No.	Air supply cu. ft. per min.	Time Minutes	Main muffle Air	Small muffle air	Litharge surface	Loss %	
1	1	21	914	809	947	1.62	Feathers
2	1	20½	947	849	975	2.06	No feathers
3	1	19½	1004	895	1012	2.75	„ „
4	1	18½	1057	944	1043	3.81	„ „

time of cupellation as well as quantity of air reaching the cupellation, but has much the lesser effect.

DIRECT AIR SERIES.

Apparatus Used.

Air was supplied through an iron tube of 5/8" inside diameter. In Fig. 20 the small muffle door, the main muffle front with attached small

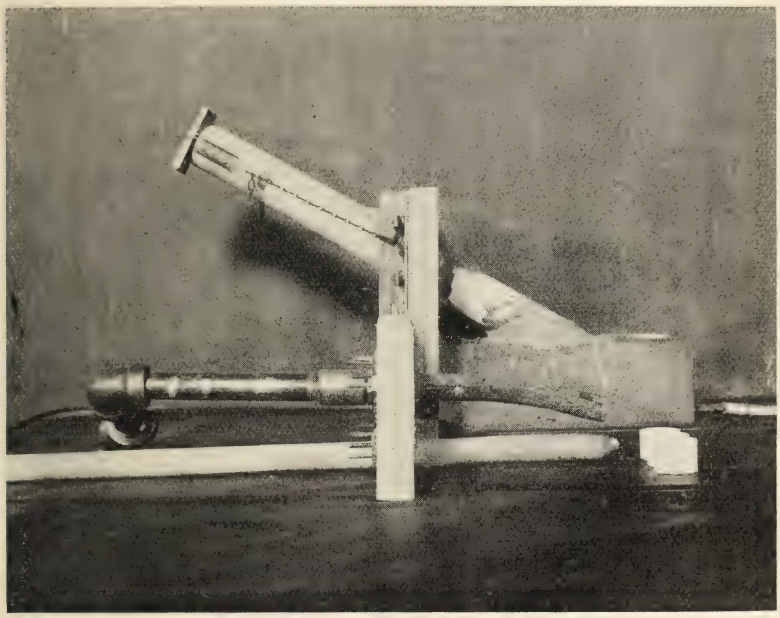


Fig. 20.

muffle and the base metal furnace couple have been removed from the furnace. The small door with its iron tube has been placed beside the small muffle, instead of inside, to show in this way the relative position of the air supply tube, cupels, and pyrometers to each other. Here the direct air tube was used instead of the diffused air box of the previous work, otherwise the apparatus was the same.

Procedure of Tests.

Here three cupels were placed as previously, but, except in one run, cupellations were made in the central one only. This was because the cupellations in the end cupels, not under direct air supply, would take much longer to finish than at the centre, and finish under dissimilar conditions. Here, also, especially in the short cupellations,

fumes came off very rapidly; to prevent these entering the optical tube it was necessary to use a suction on the main muffle. Power as before at 37 volts was utilized. Air from 1/16 to 3 cubic feet was used, and due to the shorter cupellations here, the temperatures were read every minute.

Results of Tests.

In the one run where three cupellations were done at 1½ cubic feet of air per minute, the losses from left to right were: 2.59, 3.66 and 2.37%. The central cupel finished in 8¼ minutes, the others in about 22 minutes. The average air and surface temperatures for the central cupel were: 864° C. and 1065° C. It had a heavy loss crop of feathers at the front, with scattered ones at the rear, whereas the side cupels finishing at 862° C. at no time showed feathers but gave much lower losses. The difference in loss between the outside cupels, as before, was due to the couple in front of the left one. The higher loss of the central cupel was accounted for by the greater surface temperatures resulting from the direct air supply; much more air came in contact with it than with the side cupels.

To show the effect of changing slightly the direction of the air tube relative to the cupel, one run was made with the tube pointed to direct the air under the rim of the cupel, and in the next so that the air played more on the lead. This was accomplished by merely raising the end of the pipe about one-fourth of an inch. For the first, the time was 22 minutes, loss 2.39%, average air and surface temperatures 864° C. and 1004° C. For the second the corresponding figures were 12¼ minutes, 3.87%, 871° C. and 1057° C.

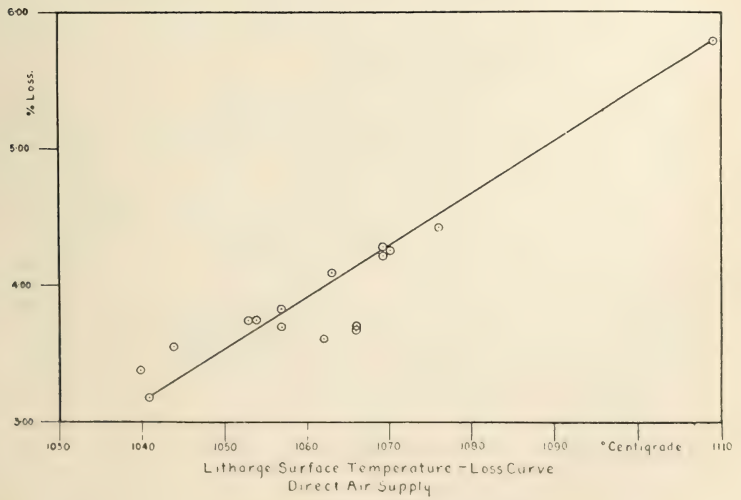
A run with 3 feet of air per minute froze at 4 minutes when not more than a gram of the button remained. At 1½ minutes a pool of litharge had formed; at 2 minutes the indicated surface litharge was 1071° C., taken amidst the dense fumes arising, while the cupel surface beside the pool of litharge was dark in color, due to the cooling effect at this high rate of direct supply. The button was reopened by increasing the temperature; the litharge began to melt at 880° C. (air temperature). The loss was 13.51%. This very high loss was largely due to the litharge pool.

The results of the series of tests using air from 1/16 cubic foot per minute up to 2 cubic feet, with the same set-up in each case, are in Table 27. The surface temperatures and loss are plotted in Curve 17. Due to the shorter cupellations here, and to the rapidly rising high end temperatures, the averages are not as representative as in longer runs; this accounts for the somewhat erratic distribution of points. A

straight line has been drawn through these, merely as a guidance in interpreting the general direction of the relation between the loss and surface temperature. Increase of air here increased surface temperature, whereas with diffused air it decreased it. These temperatures are

TABLE 27. DIRECT AIR SERIES.

			Average Temperatures				
No.	Air cu. ft. per min.	Time minutes	Large muffle air	Small muffle air	Litharge surface	Loss %	
1	1/16	14-5	958	876	1044	3.54	
2	1/16	15-05	963	876	1040	3.38	
					1057	3.87	
3	1/8	12-25	960	871	1054	3.74	
4	1/8	12-0	955	870	1066	3.69	Small feathers
5	3/16	11-25	954	870			No front stain
6	3/16	10-0	958	872	1063	4.09	No feathers
					1053	3.74	Feathers
7	1/4	9-0	963	871	1057	3.69	,,
8	1/4	8-50	946	854	1062	3.60	Feathers front
9	5/16	9-10	952	864			and back
10	5/16	8-35	961	871	1069	4.21	,,
11	3/8	7-50	952	859	1069	4.28	,,
12	3/8	8-30	960	866	1066	3.67	,,
13	1/2	7-30	962	865	1076	4.42	,,
14	1/2	9-05	945	843	1041	3.18	,,
15	3/4	7-05	963	860	1070	4.26	,,
16	1	6-05	951	852	Fumes	4.59	,,
17	2	4-0	959	819	1109	5.78	,,



Curve 17.

much higher here throughout, in spite of the fact that the cooling effect of air is chiefly focused on the alloy and top of the cupel, not on the muffle as a whole. The air has high velocity here; used air is rapidly replaced by a fresh supply, and fumes swept away, thus promoting rapid oxidation. Air has its major effect here in increasing the surface temperature.

The conditions affecting air temperatures are quite different here from those in the diffused air runs. The air fed through the tube would have less effect in cooling down the front of the muffle where the pyrometer tube was located. The cupellations were shorter. These conditions would tend to give higher temperatures. There was only one cupellation, and that not in front of the couple. This should tend to give lower temperatures, though the heat was liberated more quickly. The air temperatures were higher throughout; the main muffle temperature was little affected by changes in the air supply. If any interpretation between air temperatures and loss may be drawn, it is that the losses are increasing with the decrease in air temperature, which is contrary to any previous interpretation. It is evident that no conclusions may be safely made here. As stated several times before, the only air temperature measurements with which loss may be safely compared are those taken quite near it. This was not done here, because the tube near the cupellations would have spoiled the good diffusion of air, and if placed above the central cupel would have prevented the optical temperature measurements.

This direct air series indicates that an increase of air decreases the cupellation time and muffle air temperature, but increases the litharge surface temperatures, and the loss.

Other points worth noting were:—

(1) Beads were well attached.
(2) Blicks occurred almost immediately after the oxidation ceased.
(3) When the muffle air temperature was below 870° C., the cupels were not stained in front.
(4) Feathers formed at air temperatures up to 870° C.

Confirmatory Work.

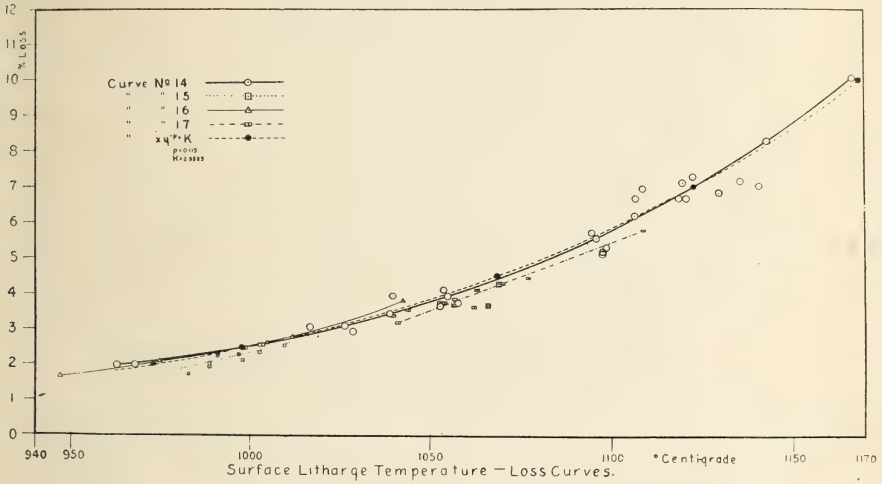
Two cupellations were made using as air supply tube an alundum pyrometer tube of 5/8" diameter with a 1/16 inch hole drilled in the closed end, and this located about 1½" in front of the cupel. Air at 1/16 cubic foot per minute was used. Lead temperatures could not be taken due to dense fumes.

On these the losses were 7.53 and 6.58%, the times 5 and 5½ minutes, the air temperatures 918 and 892° C., the main muffle tem-

peratures 986 and 963° C. The loss differences and times varied in part due to slight variation in the tube position. This shows the very high losses occurring when the main air effect is to increase the rate of oxidation, rather than cool the whole cupel or the muffle air. The amount of air was small, but it had high velocity. Due to the intensity of the reaction, the alloy moved about in the cupel.

COMBINED CURVE OF LITHARGE SURFACE TEMPERATURES AND LOSS.

On Curve 18 are plotted to one scale curves 14, 15, 16 and 17 to bring out more clearly the agreement of these over a wide range. The data for these were obtained under different conditions, such as amount



Curve 18.

and method of application of air, furnace temperature and in different furnaces. Considering this, the agreement shown is good.

Assuming Curve 14, which covers the widest range of temperature, to be the most representative, the equation $xy^{-p} = K$ has been utilized to determine the derived curve shown. By exterpolation, continuing this curve downwards, the loss at an average surface litharge temperature of 884° C. would be 0.87%. From Curve 16 the loss indicated for this temperature is 0.84%. This is of interest, because it gives some idea of the loss, were it possible to keep the surface temperature at the assumed melting point of litharge, or 884° C., without rise. In this work there was a sharp rise in the optical reading once oxidation began, of 50 or more degrees in the first minute or two. Whenever the temperature was lowered to about 915° C. freezing was imminent,

and soon occurred unless the temperature was increased at once. The advantage in practice of using coolers and cold iron over cupellations is that they reduce the litharge surface temperatures, with consequent decrease in loss. Of course, towards the end, the temperature must be allowed to rise, to ensure finishing free of lead.

The particular relation shown by the curves would not hold for different amounts of lead, or silver, or for different cupel types. The concentration of silver in lead is a controlling influence on the amount of silver that litharge will dissolve at a particular temperature. The relative per cents. of silver passing to litharge, and to the cupel as mechanical losses (absorption of lead silver alloy), are not known. The latter losses will be influenced by the shape of cupel used, the material thereof, the grain sizes and proportion of each grain size. There may be a mechanical loss of the alloy, carried off with the volatilized litharge, as well as the silver dissolved in it. Whether the silver passes to litharge wholly as oxide, or in part as silver, has not been established. The whole question is a complex. The present work shows that the total loss is closely connected with surface temperature, and that air supply is an important factor in influencing this temperature. The practical import is, that for low losses the average surface temperatures must be kept low. With the surface in view and a knowledge of the effects of air on the temperature, this is not difficult.

AVERAGE AND END TEMPERATURES.

It is general practice in comparing losses against temperatures, to take the latter at stated intervals over the process, and then average the readings to stand for the whole time. This seems to be the only practical procedure available. By this method one cupellation started at a low temperature and finished high may give the same average temperature as another where the reverse held, started high and finished low. It does not follow that the losses will agree. If the rate of loss over a whole cupellation were constant, no misconception would be introduced in thus interpreting the results; but work by the author convinced him that the loss is at a much higher rate at the end of cupellation. Bugbee (y) gives a curve, showing also that the progressive loss rate increases throughout a cupellation, and is a maximum at the end. The work to be described here was undertaken to ascertain, how much of small amounts of lead, added to silver when molten, would remain in the silver, after cupellation or oxidation if any took place, *i.e.*, could surcharges be obtained on very short cupellations.

(y) Bugbee, E.—" Text Book of Fire Assaying", 1922.

The vertical tube furnace described in Part III for the litharge experiments was used, where the cupels sat on the Cambridge resistance pyrometer tube. Close to 100 milligrams of silver was melted in a cupel at a temperature of 965-970° C. Air at 1 litre per minute was introduced through the top, which had a glass window to observe the reactions on the cupel. Fumes passed out at the bottom of the muffle tube. When the addition of amounts of lead as low as 1 milligram showed high silver losses instead of gains, it was decided to add progressively with each run, more lead, and thus ascertain the relatively high losses occurring at the end stages of cupellation.

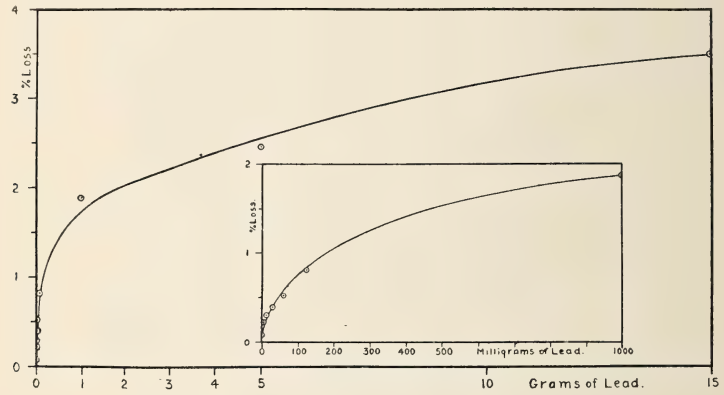
The data obtained are given in Table 28, and losses are plotted against lead in Curve 19. At no time was the temperature above 975° C. here. The work shows the high losses occurring at the end of cupellation. Whether the end temperature is high or low, during the last minutes of cupellation will have a much greater effect on the

TABLE 28.

No.	Lead added mgs.	Loss %	
1	1	0.08	
2	1	0.23	Lead added in paper,—Bead sprouted.
3	5	0.22	Black fumes emitted, no evidence of normal cupellation.
4	10	0.30	Bead bright as at the end of a cupellation, no color play.
5	25	0.40	Bead showed oxidation to litharge and color play.
6	50	0.52	Surface bright in 4 seconds, lasted 6 seconds, then dull.
7	100	0.81	Litharge worked off in patches for 32 seconds, bright for 9 seconds, then color play.
8	1000	1.88	Cupelling in 7 seconds, bright at 4 minutes, play of colors for 20 seconds; bead attached, former ones not.
9	5000	2.46	Cupelling in 20 seconds, attached bead.
10	15000	3.51	30 minute cupellation, attached bead.
11	100+ 100 PbO		
12	0	+0.01	100.24 mgs. silver melted for 10 minutes. Bead cleaned, weighed 100.25 mgs.

total silver loss, than it will on the average temperature. The thin film of fluid litharge dissolves the silver that it is capable of under the existing conditions at the moment. This is governed largely by the temperature of the surface film and the concentration relative to the volume of metal.

The concentration of silver in the lead button is lowest at the start of cupellation and progressively increases, until at the end only the silver remains. It is at the end stages when the protection of lead is least, that the losses of silver to litharge are highest. The actual temperature of the litharge at this stage when the loss rate is highest is very important in its effect on the total loss. The end temperatures of surface litharge are most difficult to take in short runs due to rapid oxidation and where the losses are highest, but as there they constitute a larger percentage of the total temperature readings than in the long runs, affect the average temperature more. This shows how unrepresentative averages may be.



Curve 19.

THE ABSORPTION OF SILVER IS GREATEST NEAR THE BEAD.

In determining where the silver absorbed by a cupel is distributed, it was found that the greatest amounts were located near the surface, and that the concentration was greatest under and close to the bead, where it is natural to expect the silver absorbed at the end of a cupellation would go. Assays of the bone ash with its absorbed litharge (stained part) were made on portions from cupels on which 1 gram of silver with 15 g. of lead had been cupelled. Table 29 shows the part of the cupel assayed, its weight and the silver recovered. In the last column the milligrams of silver per gram of cupel material are given, as a basis of comparing the absorption at the various locations. In No. 1 the surface was sand-papered, and in No. 2 the surface was scraped with a knife, roughly to a depth of ⅛". In No. 3 a 21/64" drill was passed down through the area on which the bead had been; the hole was then reamed to ½". In No. 5 a 9/16" drill was used, the tapered conical point only passing into the cupel at the bead area, to

obtain the material close around and under the bead. This showed the highest concentration of silver, followed by the top 1/64" of No. 1. The centre drilling of No. 3 shows the next highest concentration. It is again evident, then, that the greatest losses occur near the end of cupellation. This adds further emphasis to the conclusions previously made re average and end temperatures. While average temperatures seem to be the only ones which can be taken in comparing loss, interpretation based on them may be in error, due to variations throughout the cupellation, often beyond the assayer's control.

TABLE 29. LOSSES AT VARIOUS PARTS OF A CUPEL.

No.	Part of Cupel assayed.	Bone ash + litharge grams	Silver recovered mgs.	Mgs. silver per gram of cupel material
1	Top 1/64" (approx.)	1.15	2.68	2.33
	Balance.	30.45	8.32	0.27
2	Top ⅛" „	13.83	8.56	0.62
	Balance.	17.97	2.79	0.16
3	21/64" drill through bead area.	3.28	3.62	1.10
	Between 21/64" and ½" drill.	6.82	2.38	0.35
	Balance, includes some unstained ash.	27.38	6.68	0.25
4	Whole stained part.	32.92	12.62	0.38
5	Tapered point of 9/16" drill into bead area.	1.87 g.	5.34	2.86
	Balance.	29.25	7.68	0.26

SUMMARY.

A review of the work described warrants the following conclusions and recommendations:

(1) Air supplied to a muffle has these main effects.

(a) It cools the muffle, the cupel, the alloy, and the litharge. When air has its greatest effect in cooling, then the greater the air supply the lower is the loss.

(b) It increases the rate of oxidation; the heat liberated passes from the surface litharge to the alloy, the cupel, and the surrounding air. The greater the amount of air coming in actual contact with the button, the greater is the rate of oxidation. When air has its greatest effect in increasing the rate of oxidation, then the greater the supply, the greater is the loss.

These effects (a) (b) are opposed to each other, the resultant temperatures being a compromise.

(2) Loss of silver increases as litharge surface temperatures increase. After active oxidation begins, this temperature is higher than the surrounding air temperature. The absorption losses and the loss rate are highest at the end of cupellation, when the surface temperature is a maximum.

(3) Air temperatures vary, depending on where taken in the muffle, and are not a reliable guide to loss unless taken close to the actual cupellation. With a constant air supply, loss increased directly with increase of air temperatures, so taken.

(4) The time of cupellation varies inversely as the air supply, and its temperature; the former has the greater effect. In general, increasing time decreased loss. In Table I, Part V, this relation did not hold.

(5) With constant air supply, the percentage loss of silver,

(a) Increased as lead in the buttons was increased.

(b) Decreased as silver in the buttons was increased.

(6) Frozen buttons gave very unreliable results, and litharge pools gave high and varying losses. With assay litharge only, in contact with silver, very high losses occurred, but with lead present these were decreased. Buttons should be melted at a temperature where they quickly open, as delayed opening increased losses.

(7) Feathers are not always a reliable indication of low loss; they were present when high losses cocurred, due to a high draft. A crop of short close feathers indicated a high draft.

(8) Undiluted oxygen increased loss; nitrogen mixed with air gave low but erratic losses.

(9) Irregular air supplies, and eddies, gave irregular losses. Muffle draft varied greatly with furnace adjustments and with flue draft.

(10) Air should be drawn through the muffle independently of the natural flue draft, preferably by a suction fan capable of adjustment, to suit the work at hand. Each assayer can establish the conditions most suitable for his work.

(11) Air should be admitted to the muffle in a uniform manner across the entire width, and be exhausted similarly, to promote the same flow of air to all cupels. The speed and direction of fumes is a general guide to the amount of air reaching a cupellation, and its velocity.

(12) The heat supplied to a muffle from front to rear should be so adjusted, that with the distribution of air present, the cupelling buttons appear to be of similar temperature throughout; this promotes uniformity of loss.

(13) Cupels should be the same height and be placed close together, with their tops level.

A smooth surfaced fire bar of uniform height and cross-section should be used in front of the cupels in preference to dummy cupels. It acts as a heat reservoir, protecting the cupels from undue cooling by direct air impringement.

(14) Deep cupels, hoods, and rings reduced the rate of oxidation and decreased the loss. Deep cupels of over capacity for the buttons are recommended where low losses are desired, but they give slow cupellations.